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New Orleans, Louisiana, November 1983 Volume 1

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# PROCEEDINGS: EIGHTH SYMPOSIUM ON FLUE GAS DESULFURIZATION NEW ORLEANS, LA, NOVEMBER 1983

## Volume 1

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16. ABSTRACT The proceedings document the eighth in a series of symposiums (the second consponsored by EPA and the Electric Power Research Institute) on flue gas desulfurization (FGD). It provided a forum for the exchange of technical developments and regulatory information on FGD systems and processes applicable to utility and industrial boilers. The keynote address described the National Acid Precipitation Assessment Program. Other opening-session presentations were on the status of air quality legislation/regulations, the status of solid waste regulations, and trends in commercial application of FGD technology. Subsequent sessions dealt with FGD economics, materials of construction, dry furnace absorbent injection, dual alkali FGD, flue gas treatment (combined SOx/NOx removal), FGD chemistry, the architect-engineer's role in FGD applications (panel discussion), limestone/organic acid, waste disposal/utilization, and dry FGD systems. Participants represented electric utilities, equipment and process suppliers, state environmental agencies, coal and petroleum suppliers, EPA and other federal agencies, and research organizations.

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| a. DESCRIPTORS | | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group | |
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| Flue Gases | Calcium Carbonates | Stationary Sources | 21B | |
| Desulfurization | Organic Acids | Acid Precipitation | 07A, 07D | 07C |
| Waste Treatment | | | | |
| Economics | | | 05C | |
| Sulfur Oxides | | | 07B | |

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# PREFACE

These proceedings for the Eighth Symposium on Flue Gas Desulfurization constitute the final report submitted to the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park (IERL-RTP), North Carolina, and to the Coal Combustion Systems Division, EPRI, Palo Alto, California. The symposium was conducted in New Orleans, Louisiana, November 1 to 4, 1983.

This symposium was designed to provide a forum for the exchange of technical and regulatory information and developments on the systems and processes applicable to utility and industrial boilers. In the opening session, a keynote address was given on the status and outlook for the national acid precipitation assessment program. Presentations were also made on the status of air quality legislation and regulations, the current and projected regulations of the resource conservation and recovery act, and trends in commercial application of flue gas desulfurization (FGD) technology. There were subsequent technical sessions on economics, materials of construction, dry furnace absorbent injection, dual-alkali, flue gas treatment (combined $SO_x/NO_x$) removal, the role of the architect-engineer as the middleman between the utility and FGD supplier (discussion), FGD chemistry, limestone/organic acid, waste disposal/utilization, and dry FGD systems, pilot plant test results and full scale installations. Participants represented electric utilities, equipment and process suppliers, state environmental agencies, coal and petroleum suppliers, EPA and other Federal agencies, and research organizations.

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## SESSION 1: OPENING SESSION

Chairman: Julian W. Jones
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC

# National Acid Precipitation Assessment Program: Status and Outlook

J. Christopher Bernabo
Executive Director
National Acid Precipitation
Assessment Program
722 Jackson Place, NW
Washington, DC 20506

The National Acid Precipitation Assessment Program is designed to successively improve our understanding of the causes, effects and possible solutions to the acid rain problem. The Program includes research, monitoring and assessment activities that emphasize the timely development of a progressively firmer scientific basis for decision making by the Congress, regulatory agencies, private sector managers, environmental groups, and the public. The National Program consists of over 200 projects and hundreds of scientists in government, academia, and the private sector.

## LEGISLATION AND ORGANIZATION

The Interagency Task Force on Acid Precipitation was established by the Acid Precipitation Act of 1980 (Title VII of the Energy Security Act: P.L. 96-294) to oversee the planning and implementation of the National Acid Precipitation Assessment Program. Prior to the passage of the Acid Precipitation Act of 1980, several Federal agencies were sponsoring acid rain research, but more in a piecemeal fashion than a coordinated program. The Acid Rain Coordinating Committee (ARCC), which was established in 1980, was an attempt to organize the ongoing Federal efforts. After the Act passed, the ARCC was reconstituted,and provided the foundation upon which the statutory National Acid Precipitation Assessment Program was established.

The Task Force is jointly chaired by the Environmental Protection Agency (EPA), the Department of Agriculture (USDA), and the National Oceanic and Atmospheric Administration (NOAA). The Council on Environmental Quality serves as the Executive Secretary of the Task Force. The remaining members include one high-level representative from each of the other eight Federal entities in the Program: the Departments of Energy (DOE), Interior (DOI), Commerce (DOC), Health and Human Services (HHS), and State (DOS); the National Aeronautics and Space Administration (NASA); the National Science Foundation (NSF); and the Tennessee Valley Authority (TVA). The Task Force also includes the directors of Argonne, Brookhaven, Oak Ridge and Pacific Northwest National Laboratories, as well as four Presidential appointees.

The Task Force itself functions as the "board of directors" for the National Program by setting the research goals, identifying the projects needed to meet these goals, and deciding which agencies are best suited to conduct the necessary work.

In addition, the primary responsibilities to the Task Force are to:

- Plan and manage the National Acid Precipitation Assessment Program.
- Provide annual reports on the National Program's progress.
- Produce an annual interagency budget for the National Program.
- Coordinate the National Program with the research and monitoring activities of the private sector groups, environmental organizations, states, and other nations.
- Maintain an inventory of Federally-funded acid deposition research projects.
- Disseminate research results, and assessments of their implications.

The Task Force has 10 working-level Task Groups, one for each of the National Program's nine research categories and one for international activities. These technical groups include program managers and experts from all the participating Federal agencies and National Laboratories. They are responsible for the detailed planning and research in their assigned areas. The Task Groups with their Coordinating Agencies are:

| Task Group | Coordinating Agency |
|---|---|
| A. Natural Sources | NOAA |
| B. Man-made Sources | DOE |
| C. Atmospheric Processes | NOAA |
| D. Deposition Monitoring | DOI |
| E. Aquatic Effects | EPA |
| F. Terrestrial Effects | USDA |
| G. Effects on Materials and Cultural Resources | DOI |
| H. Control Technologies | EPA |
| I. Assessments and Policy Analysis | EPA |
| J. International Activities | DOS |

The Research Coordination Council (RCC) oversees and integrates the efforts of the various Task Groups, and develops draft reports, program plans, budgets and other recommendations for consideration by the full Task Force. The joint chairs designated the Task Force's executive director to chair this council. The RCC includes leaders of all the Task Groups, the chairperson of the National Laboratory Consortium, and other appropriate agency representatives.

## Budget Process

The Task Force developed its first interagency budget for the Program in January, 1981 and submitted it to Congress as part of the President's FY 1982 budget request. The role of the Task Force in planning the interagency budget for the National Program is a highly effective and unique aspect of the Federal effort. During this interagency budget process, the Task Force receives initial guidance on the target funding levels for the total program; it then advises the individual Task Groups of the anticipated increases (or decreases). Using this as guidance, the Task Groups adjust their research plans or suggest new initiatives, as appropriate, for the target funding levels. The Task Groups present their budget package to the Task Force for review and approval. From this the Task Force develops and submits its interagency budget recommendations; the agency budget requests are thus reviewed as part of an integrated multiagency program.

By working together through the Task Force, the agencies have established a research program that addresses national needs while building on the research expertise of the individual agencies. This strong interagency planning process ensures an integrated and comprehensive program, with each agency contributing to specific aspects of the overall national effort.

The interagency budget for the National Program does not include Federal funds for control technology hardware development because control technology activies are conducted under preexisting programs at EPA, DOE, and TVA. The National Program is actively coordinating with the relevant ongoing Federal control technology efforts to ensure that the concerns relative to acid deposition are addressed.

The Task Force is vigorously implementing the comprehensive national research program. The interagency budget for the National Program was $17.4 million in FY 1982, $22.3 million in FY 1983 (Figures 1, 3, & 4), and $27.5 million has been requested for FY 1984 (Figure 2). Federally-funded acid deposition research has doubled from about $11 million in FY 1980 to $22.3 million for FY 1983, and the President's budget for FY 1984 requests a further 24% increase in funding (Figure 5). The National Program is producing results at an increasing rate, and disseminating them as soon as they become available.

## Annual Report

By law the Task Force is required to issue an annual report to the President and Congress describing the progress of the National Program. The Task Force's first annual report was issued in January, 1982; with research barely underway, the report discussed primarily the development of the management structure, and the initial implementation of the Program.

Figure 1

## NATIONAL ACID PRECIPITATION ASSESSMENT PROGRAM

FY 1983
($ in thousands)

| | | DOA | | | | DOI | | | |
|---|---|---|---|---|---|---|---|---|---|
| | EPA | SR | FS | NOAA | DOE | FS | GS | FW | TOTAL |
| A. Natural Sources | | | | 700 | | | | | $ 700 |
| B. Man-made Sources | 1050 | | | | 300 | | | | 1350 |
| C. Atmospheric Processes | 3858 | | | 1050 | 274 | 50 | | | 5232 |
| D. Deposition Monitoring | 1145 | 404 | 145 | 500 | 666 | 100 | 1449 | | 4409 |
| E. Aquatic Effects | 1935 | | 210 | | 550 | 148 | 445 | 75 | 3363 |
| F. Terrestrial Effects | 1468 | 946 | 1258 | | 50 | 229 | 486 | | 4437 |
| G. Effects on Materials | 410 | | | | | 535 | 50 | | 995 |
| H. Control Technologies | (7600)* | | | | (6500)* | | | | (14,100)* |
| I. Assessments and Policy Analysis | 1570 | | | | 220 | | | | 1790 |
| Subtotals: | | 1350 | 1613 | | | 1062 | 2430 | 75 | |
| TOTALS: | $ 11,436 | 2963 | | 2250 | 2060 | | 3567 | | $ 22,276 |

* Control Technologies figures not included in total. These funds for general development of $SO_2$ and $NO_x$ control hardware are appropriated under other preexisting programs. The Control Technologies Task Group coordinates these efforts with the assessment and research activities of the National Program.

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Figure 2

## NATIONAL ACID PRECIPITATION ASSESSMENT PROGRAM

Proposed revisions to the President's Budget Request (May 1983)

FY 1984
($ in thousands)

<table>
<tr><th></th><th></th><th colspan="2">DOA</th><th></th><th></th><th colspan="4">DOI</th><th></th></tr>
<tr><th></th><th>EPA</th><th>SE</th><th>FS</th><th>NOAA</th><th>DOE</th><th>FS</th><th>GS</th><th>FW</th><th>BLM</th><th>TOTAL</th></tr>
<tr><td>A. Natural Sources</td><td></td><td></td><td></td><td>955</td><td></td><td></td><td></td><td></td><td></td><td>$ 955</td></tr>
<tr><td>B. Man-made Sources</td><td>1090</td><td></td><td></td><td></td><td>260</td><td></td><td></td><td></td><td></td><td>1350</td></tr>
<tr><td>C. Atmospheric Processes</td><td>5250</td><td></td><td></td><td>1020</td><td>270</td><td></td><td></td><td></td><td></td><td>6540</td></tr>
<tr><td>D. Deposition Monitoring</td><td>1789</td><td>274</td><td>146</td><td>1130</td><td>942</td><td>122</td><td>1870</td><td></td><td>80</td><td>6353</td></tr>
<tr><td>E. Aquatic Effects</td><td>2285</td><td></td><td>210</td><td></td><td>550</td><td>148</td><td>445</td><td>125</td><td></td><td>3763</td></tr>
<tr><td>F. Terrestrial Effects</td><td>1468</td><td>946</td><td>1258</td><td></td><td>50</td><td>229</td><td>486</td><td></td><td></td><td>4437</td></tr>
<tr><td>G. Effects on Materials</td><td>605</td><td></td><td></td><td></td><td></td><td>740</td><td>150</td><td></td><td></td><td>1495</td></tr>
<tr><td>H. Control Technologies</td><td>(4100) *</td><td></td><td></td><td></td><td>(7000) *</td><td></td><td></td><td></td><td></td><td>(11,100) *</td></tr>
<tr><td>I. Assessments and Policy Analysis</td><td>1500</td><td></td><td></td><td></td><td>1175</td><td></td><td></td><td></td><td></td><td>2675</td></tr>
<tr><td>Subtotals:</td><td></td><td>1220</td><td>1614</td><td></td><td></td><td>1239</td><td>2951</td><td>125</td><td>80</td><td></td></tr>
<tr><td>TOTALS:</td><td>$ 13,987</td><td colspan="2">2834</td><td>3105</td><td>3247</td><td colspan="4">4395</td><td>$ 27,568</td></tr>
</table>

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* Control Technolgies figures are not included in totals. These funds for general development of $SO_2$ and $NO_x$ control hardware are appropriated under other pre-existing programs. The Control Technologies Task Group coordinates these efforts with the research and assessment activities of the National Program.

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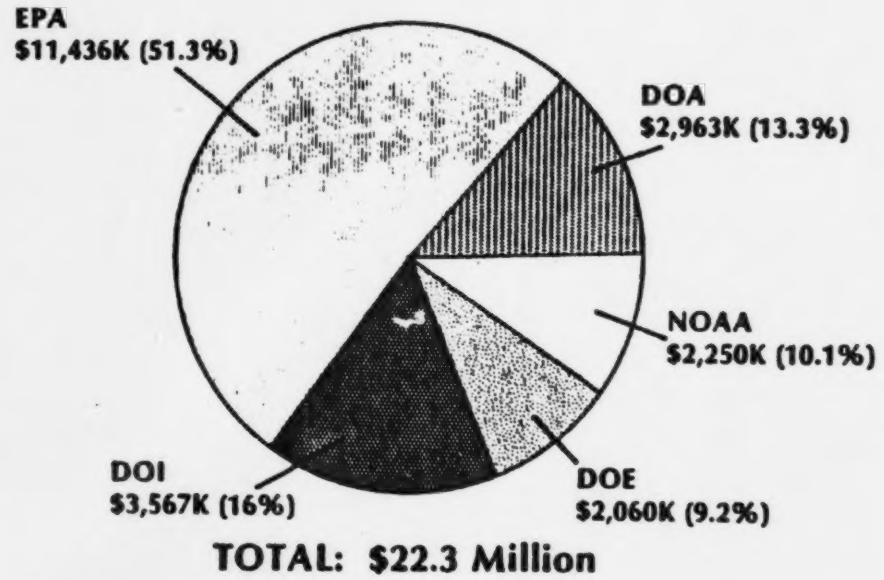
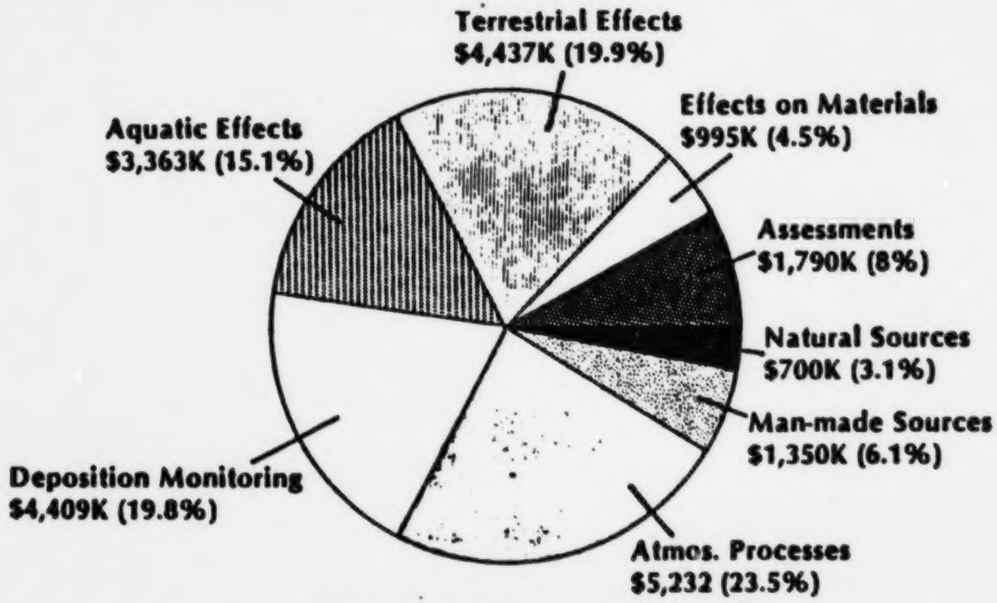
# National Acid Precipitation Assessment Program



Fiscal year 1983 funding by agency.

Figure 3

## National Acid Precipitation Assessment Program

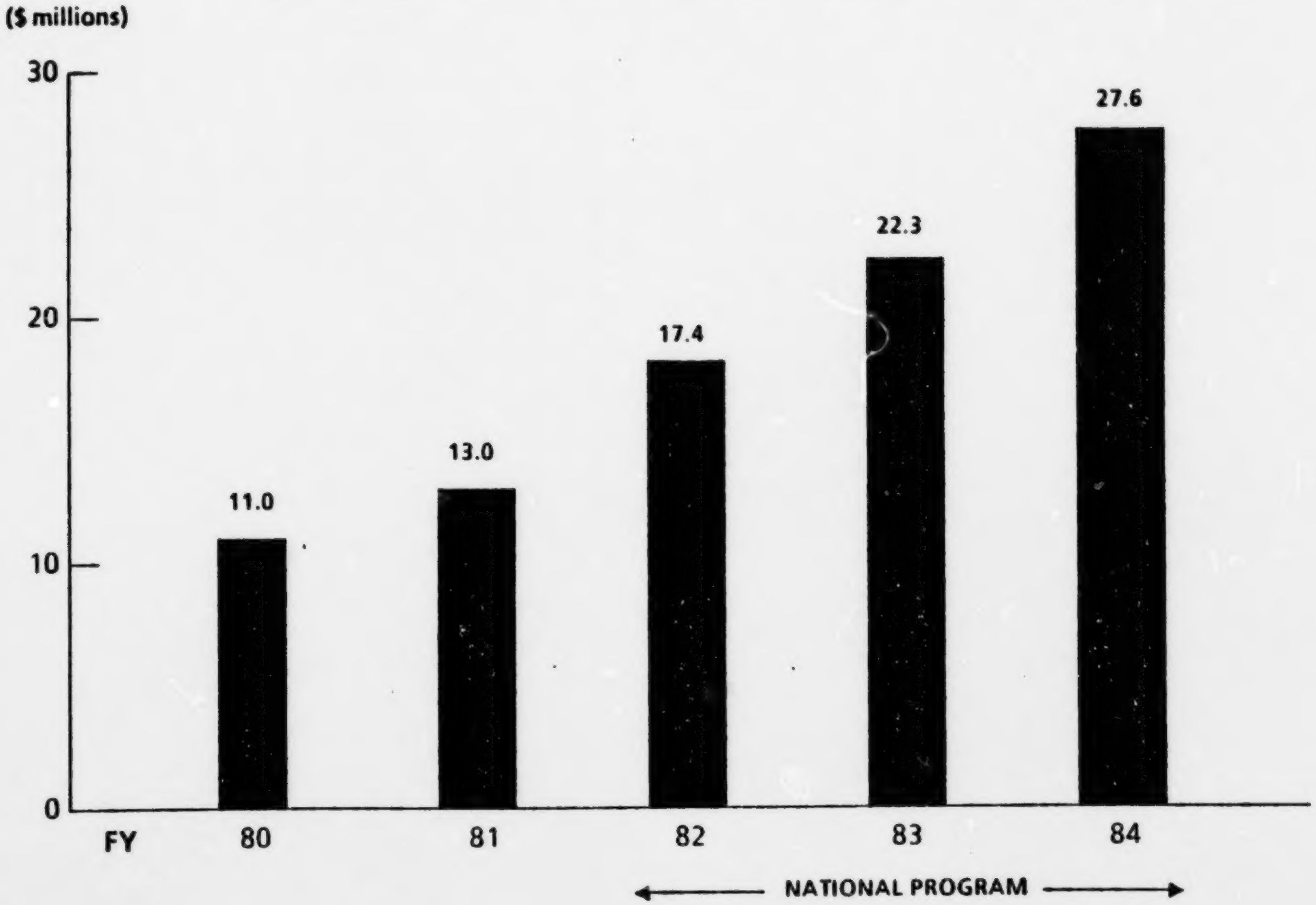


**TOTAL: $22.3 Million**

**Fiscal Year 1983 funding by research category.**

Figure 4

FIGURE 5. FEDERAL ACID DEPOSITION RESEARCH FUNDING HISTORY



In June of this year the National Acid Precipitation Assessment Program issued the FY 1982 annual report to the President and Congress on its first full year of research. The report summarizes the status of scientific knowledge, the major research findings and accomplishments of the National Program's first year, and the outlook for continued progress. As the National Program progresses, future annual reports will provide new findings and increasingly better information to assist decision makers and the public in continuing to resolve the acid rain issue.

## NATIONAL PROGRAM MANAGEMENT ACTIVITIES

In addition to internal planning and management activities, the Task Force meets with representatives of key non-Federal groups conducting acid deposition research and monitoring activities. The Task Force is committed to conducting a National Program that coordinates the Federal efforts with the activities of the states, private sector groups, research institutes, environmental groups, and other countries, especially Canada. Several specific steps have been taken to develop and encourage such cooperation and more extensive joint planning activities are anticipated. Such activities include:

### National Plan Workshop

Besides a public review of the draft plan of the National Program, the Task Force's April 1981 workshop of non-Federal experts began a dialogue with state and private groups. The workshop report describes the participants' ideas concerning how coordination and cooperation can best be accomplished. The Task Force is implementing many of these suggestions and is actively pursuing continued exchanges of information with non-Federal groups.

### Annual Meeting

The Task Force holds an annual meeting for program participants to assess research progress, to propose future work, and to assess the implications of existing information. The meeting provides a mechanism to bring together the full spectrum of research managers and scientists to fascilitate dialogue about the National Program and foster integration of its various elements, and thus enhance program unity.

The next annual meeting is proposed for January 16-19, 1984 with the theme being "research to meet policy needs". This meeting will be an effort to educate decision makers on the capabilities and the limitations of the National Program's research and assessment activities, as well as a prime opportunity to get feedback on the needs of the decision makers. In addition to members of the Task Force, the invited participants will include senior congressional staff; representatives from states, private sector and environmental organizations; and key scientists.

## Federal-State-Private Sector Coordination

The Task Force initiated and encouraged joint sponsorship of an Acid Deposition Research Coordination Workshop in November 1982. The non-Federal sponsors included the Electric Power Research Institute, the American Petroleum Institute, the Gas Research Institute, the Coordinating Research Council, and the National Council of the Paper Industry for Air and Stream Improvement. Environmental groups and states were also invited to participate.

The purpose of the workshop was to bring together key Federal and non-Federal managers of acid deposition research to review and discuss the management and coordination of their research planning efforts. Specifically, the two goals of the meeting were (1) to assess the scope of the nationwide acid deposition research effort, and (2) to initiate a continuing process for joint planning and coordination of Federal and non-Federal acid deposition research efforts.

In addition to developing joint statements on research needs and disseminating information, the state representatives agreed to organize by regions and to define their specific areas of expertise. The Task Force agreed to investigate ways to increase opportunities for state and private sector participation in reviewing the National Program. Follow-up activities include further discussion between the Task Force, and the private sector and state representatives to work out the details.

Since the workshop, National Program representatives have participated in several meetings with the states to help identify the specific research needs of the region, and to encourage the states to develop research programs on acid deposition. Initial plans nave also been made for a follow-up meeting with the original participants and others.

## National Program Research Peer Reviews

An integral part of the sound management of the National Program is periodic peer reviews by a panel of outside experts. These detailed scientific reviews allow the National Program's research to be examined in a comprehensive manner rather than as a series of discrete agency projects, and provide the opportunity to assess the quality of the science. More specifically, the reviews are designed to:

- o provide an opportunity for National Program researchers to report on progress, and to present research results and major findings;
- o facilitate the exchange of information, and enhance cooperative research among scientists involved in the Federal program and others;
- o provide an opportunity for those outside the Federal government to review and comment on the evolving National Program; and
- o assist research managers in providing adequate program coordination and research direction.

## U.S.-Canadian Research Program Cooperation

In April 1982 and July 1983, Task Force representatives met with the Canadian Federal/Provincial Research and Monitoring Coordinating Committee (RMCC) to expand bilateral scientific cooperation. Leaders of both the U.S. and Canadian research efforts emphasized the mutual value of greater cooperation and coodination of activities. The highlights of the July 1983 meeting include synopses of all bilateral acid deposition research projects currently underway, as well as listings of suggested projects to be undertaken jointly by the two countries in the future. The Task Force representatives feel that much of the suggested research is promising, and the National Program is now using the list of suggested projects in setting its research priorities for the FY 1985 budget process.

The 25 to 30 invited reviewers are chosen from the leading scientists in the United States, Canada and other nations. They critically evaluate all the research to ensure that each project contributes to the identified objectives, milestones, and deliverables, and they assess the research progress and plans as well as make recommendations to guide future research.

The review of aquatic and terrestrial effects research was held in February 1983, and the review of sources, monitoring and atmospheric processes research was held in August 1983. The review of assessment activities is proposed for February, 1984.

## Inventory of Acid Rain Research Projects

Project descriptors for all the Federally-funded research were entered into the computor this spring, and are presently being verified by each Task Group leader. The inventory includes information on all ongoing projects with the performer(s), duration, funding, study area, research goals, methodologies, and expected outputs. With the Federal research projects on-line, work can begin in FY 1984 on the inventory of all state-sponsored research and monitoring acitvities. The computer inventory will be maintained and updated for use by the Task Force, and all interested parties. The private sector has conducted a similar inventory of its activities; together with the Task Force's effort, this should provide a complete catalog of all acid deposition research and monitoring activities in the United States.

## Information Dissemination

The National Program served as the catalyst and hosted a meeting on acid rain information sources in October, 1983. This meeting brought together sponsors, producers and users of bibliographies and research project inventories on acid rain. Presentations were made on the status and outlook for these services, with the focus on the scope and purpose, dissemination availability, and identification of user needs. The interaction between the participants was encouraging, and greater cooperation is anticipated for the future.

## MAJOR RESEARCH QUESTIONS

The National Program includes research, monitoring, and assessment activities to develop answers to major research questions. In addition to identifying and reducing scientific uncertainties, the National Program is organizing the scientific information to address policy questions. The Task Force is establishing a systematic framework for evaluating costs and benefits of alternative policy options for controlling man-made sources of acidity or mitigating adverse effects.

Some of the overall research questions the National Program is specifically addressing are given here with some indication of the type of work underway to answer the questions.

1. **Does acid deposition significantly affect aquatic resources, crops, soils, forests, materials, or human health?** Except for poorly-buffered lakes, evidence on other actual impacts is inconclusive. The National Program includes intensive laboratory and field studies to develop a more definitive understanding of the potential for damage to sensitive resources.

2. **Where are the sensitive resources? How much damage has occurred, or how long will it take for damage to occur?** Concern about acid deposition centers around its potential and known effects. The National Program is developing inventories of the aquatic, terrestrial, and cultural resources at risk, and is surveying the resources that have already been affected by acid deposition.

3. **What is the relative contribution of wet versus dry deposition of acids?** Dry deposition may constitute up to 50 percent or more of acidifying substances, but reliable methods for its routine collection do not yet exist. Vigorous efforts are underway in the National Program to develop appropriate techniques for adequately monitoring dry deposition on a routine basis. In the meantime, interim methods for collecting dry deposition will be used to provide the best currently available data.

4. **What is the relative importance of local versus distant sources in controlling the acidity of deposition at a given location?** Neither models nor measurements currently address this question with a resonable degree of confidence. The National Program includes a broad atmospheric sciences effort with models, experiments, and measurements in the field and laboratory designed to improve our understanding of source/receptor relationships as rapidly as possible. Information on the characteristics and magnitude of man-made emissions is being redefined as well.

5. **What is the relative contribution of man-made versus natural sources of acid-forming materials?** Significant natural sources exist, but their role is uncertain. The amount of natural acid precursors arising from sources such as oceans and marshes is being determined by the National Program to assess their contribution to acidity over North America. The magnitude, distribution and character of man-made emissions are also being investigated to more accurately identify their contribution to acid deposition.

**6. What is the temporal and spatial distribution of acid deposition?** Monitoring efforts before 1977 were fragmented and inadequate for determining trends. A National Trends Network with standardization and quality control has been established to answer these questions. Using a variety of information sources, research is also underway to improve monitoring techniques and to decipher any past trends.

**7. What changes in deposition would result from a given change in sulfur dioxide, nitrogen oxides, organics, and/or primary sulfate emissions?** Scientists cannot precisely calculate the amount of emission reductions that would be required to reduce acid deposition below a particular level within a given area. We need to know more about atmospheric processes to accurately quantify source/receptor relationships. The National Program's assessment activities integrate information on sources and atmospheric processes to address this question.

## NATIONAL PROGRAM ACCOMPLISHMENTS

Some selected highlights of progress in the past two years (FY 1982 and 1983) for the National Program's research areas are as follows:

### A. Natural Sources

- Delivered the budget survey of natural sulfur and nitrogen emissions required for the transport/transformation modelers of atmospheric processes.

- Developed and tested instruments for reliable field measurement of sulfur and nitrogen emissions from natural sources.

- Continued flux measurements of natural sulfur compounds in the ocean that suggest that emissions from marine sources may contribute significantly to atmospheric acidity in some areas.

### B. Man-made Sources

- Completed preliminary study on emissions sources which suggested that nearby petroleum combustion, as well as local and distant coal combustion, could significantly affect local acid deposition.

- Continued development of models to predict the cost and emissions changes from utilities and industries based on various possible control strategies.

- Continued to develop emissions inventories for testing the transport/transformation models with improved spatial, temporal, and source-type resolution, and initiated studies to better characterize the man-made sources of acid precursor pollutants.

### C. Atmospheric Processes

- Improved understanding of atmospheric transport, cloud processes and scavenging processes.
- Initiated major field experiment to track the movement of tracer gases released in the Midwest and Canada over hundreds of miles.
- Improved atmospheric models and applied them to gain a better understanding of the movement and conversion of pollutants, and the deposition of acidic material.
- Improved empirical techniques for assessing source/receptor relationships, dry deposition of SOx and NOx gases and particles, and the transport of sulfur and nitrogen across North America.

### D. Deposition Monitoring

- Produced the first comprehensive maps describing the distribution of major chemical species over North America.
- Established the National Trends Network for measuring background quantities of wet acid deposition products.
- Developed prototype equipment and procedures for routine monitoring of dry deposition.
- Improved methods for field checks of pH and conductivity on low-concentration solutions.

### E. Aquatic Effects

- Produced a nationwide map and regional maps of the Northeast, Southeast, South Central, and Upper Midwest, indicating areas where surface waters are likely to be most sensitive to acidification.
- Began long-term study of causal relationships of acidic effects on biota for twenty sensitive watersheds.
- Completed preliminary survey of drinking water in the Northeast that indicates some reservoirs and their watersheds have limited ability to buffer acid deposition.
- Took lake core sediment samples to examine historical patterns of deposition.
- Improved understanding of factors controlling the susceptibility of surface waters to acidification, and improved methods to quantify, assess, and show trends of acid deposition effects.

- Provided research information for predicting acidification of water bodies, and for assessing potential effects of liming to restore or mitigate acidification damage.

## F. Terrestrial Effects

- Reported on the use of models to predict changes in forest growth due to acid deposition.

- Initiated extensive long-term studies to determine whether acid rain has caused changes in rate of growth and species composition in forests; also, reported on assessment of tree ring data for chemically acid environments.

- Screened forest, range and agricultural crops for greater sensitivity to disease, insect damage, and vulnerability to acid deposition.

- Performed studies in the Southeast, mid-Atlantic coast, and Northeast on soil nutrient mobilization factors related to changes in acid deposition.

- Completed several studies showing that forest ecosystems alter the acidity of rain traveling through them.

- Examined importance of dry deposition to increasing acidity throughout the forest canopy, and the response after introduction into the surface waters of the nearby watershed.

## G. Effects on Materials and Cultural Resources

- Began work to determine possible acid-deposition-related damage to historical monuments.

- Completed tombstone studies to estimate historical rates of deterioration.

- Installed simple deosition monitoring devices to determine damage to historical and other materials in the urban environment.

- Began analysis of available materials deterioration data and started documenting performance of possible protective treatments for masonry.

- Designed a field survey for delineation of materials at risk across the country.

## H. Control Technologies (Relevant efforts performed by other programs in in coordination with National Program concerns)

- Tested limestone injection multistage burner system (LIMB) that showed a decrease of 50 percent in sulfur dioxide and nitrogen oxides emissions for retrofitted burners and 70 percent for new facilities.

o Developed burner systems to decrease nitrogen oxides emissions by 75 percent in large coal-fired boilers.

o Began studies of coal cleaning practices, engineering costs of control technologies, directly emitted acidic materials, integrated control systems, and passive (non-hardware) control systems.

## I. Assessments and Policy Analysis

o Prepared the "Critical Assessment Document: The Acidic Deposition Phenomenon and Its Effects" with chapters reviewing acid deposition and its impacts with contributions from 54 scientists from many institutions in this country and abroad. The document is now undergoing final revision.

o Prepared advanced methods for integrated assessment linking all components of transport within and exchanges among relevant systems and receptors, over time and space.

o Developed analytical and statistical frameworks for increasingly complex modeling assessments, including cost-benefit comparisons.

o Developed the preliminary version of a model for assessing sulfur dioxide emissions from the utility sector, and developed empirical assessment techniques for use until reliable models of source/receptor predictions are delivered.

o Began investigation of estimating uncertainty in models and the implications for formulating control strategies.

o Assembled data bases on the quantity, sulfur content, heating value, ash content and desulfurization potential of U.S. coals to aid in evaluation of emission control strategies.

o Evaluated advanced simultaneous sulfur dioxide/nitrogen flue gas treatment processes for cost and performance relationships, and identified possible emerging processes such as electron beam irradiation.

o Improved wet flue gas desulfurization process by increasing efficiency of removal, reagent utilization, reliability and waste product disposal.

o Investigated the effectiveness of spray dryer flue gas desulfurization systems along with the bnefits of fabric filters and electrostatic precipitators.

## J. International Activities

o Continued to cooperate with Canadian counterparts for joint research proposals.

- Published "International Directory of Acid Rain Researchers", listing 1,000 scientists in 32 countries.

- Continued to compile international research information on acid deposition activities worldwide.

More details of these and other recent accomplishments in the various research categories will be contained in the FY 1983 Annual Report of the National Acid Precipitation Assessment Program.

## OUTLOOK FOR RESEARCH: FY 1985 to 1989

In the next several years the research under the National Program will produce a number of important results. The following are some highlights of specific accomplishments the National Program can produce by FY 1989.

### A. Natural Sources

- Develop an experimental data base that characterizes the natural emissions of sulfur, nitrogen, chlorine, and alkaline emissions (ammonia and others) on both a national/global and regional scale.

### B. Man-made Sources

- Update the emissions inventory to an FY 1984 base year.

- Add hydrogen fluoride, hydrochloric acid, ammonia and other alkaline substances to the inventory. Also add volatile organic compounds (VOC) by reactivity class, and disaggregate amounts of sulfur and nitrogen compounds as necessary.

- Refine, test, and operate the man-made emissions model for the 1987 and 1989 Assessments.

### C. Atmospheric Processes

- Provide a definitive mass balance for compounds of sulfur and nitrogen in North America.

- Provide a model capable of assessing localized (mesoscale) rates of wet and dry deposition from nearby sources, and develop an advanced model capable of improving assessment methods.

- Develop techniques for measuring dry deposition products that contribute to acidification.

- Conduct a major air transport experiment to help define long-range patterns of distribution and rates of atmospheric conversion to acidifying substances, for example, conversion patterns of $SO_2$ and $SO_4$ downwind of major industrial areas.

- Conduct basic research on cloud processes that affect formation of acidifying substances.

### D. Deposition Monitoring

- Addition of dry deposition monitoring into the National Trends Network (NTN) protocol, as well as trace metals and select organic substances.

- Expansion of the NTN and Global Trends Network to provide more reliable patterns of acid deposition.

### E. Aquatic Effects

- Develop recommendations for liming acidified water bodies.

- Develop and validate biological response models assessing effects of acidification over a range of loading rates and terrestrial conditions.

- Report on health effects, fish populations at risk, drinking water responses, and waterfowl effects as these relate to acid deposition.

### F. Terrestrial Effects

- Update reports on acid deposition effects on soils, especially soil-nutrient changes, and mobilization of aluminum and other metals; also, forest species effects; and responses of soybeans, corn and other crops.

- Complete a series of experiments and effects determinations to examine the enhanced susceptibility of agricultural and forest crops to disease and reduced yields.

### G. Effects on Materials and Cultural Resources

- Provide damage functions with acceptable levels of confidence for materials exposure to SOx, NOx and ammonia.

- Recommend protection methods for materials at risk as an alternative to stringent controls.

- Complete materials inventories for the United States.

### H. Control Technologies

- Report on control of directly emitted acidic materials, control of volatile organic compounds, industrial process controls, and state-of-the-art reports on control technologies.

- Evaluate passive (non-hardware) control strategies, and combinations of low cost control options, such as limestone injection multistage burner system (LIMB) and load dispatching, to attain goals.

## I. Assessments and Policy Analysis

- Develop sophisticated source/receptor assessment models, combining control and effects mitigation to integrate overall National Program modelling inputs.

- Devise and perfect decision analysis methods combining cost and benefit data for effectively managing acid deposition.

- Devise optimal scientifically-sound strategies for managing national acid deposition control programs.

## J. International Activities

- Continue and expand the cooperation with foreign countries and international resources of acid deposition research.

The National Acid Precipitation Assessment Program made an ambitious start and broad progress during its first two years of research (FY 1982 and 1983). It will take a systematic effort over a number of years to adequately address the major uncertainties about the causes, effects, and management of acid deposition. The Program has laid the groundwork for continued scientific advancement, and a framework has been established to focus the research on answering the questions most critical for developing sound policies. The National Program's recurring assessments will provide a successively refined scientific basis for decision making, and the opportunity to reexamine research directions throughout the 1980's.

# REMARKS

By: Sheldon Meyers
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I intend to deal simply and directly with my assigned topic today which is "The Status of the Clean Air Act Reauthorization." My simple and direct status report to you is that the Clean Air Act Reauthorization is as yet unenacted.

Now that I have succinctly dealt with my assigned topic, I can go on to other things.

What I would really like to do is shed some light on why the Congress has not acted on the Reauthorization so far, and suggest to you some of the reasons that this assignment is so difficult and tricky. I would also like to identify some of the areas of the Act that are causing us at EPA to have sleepless nights and develop prematurely gray hair, by reciting some of the elements which should be included in any discussion of a reauthorization.

Unfortunately, I don't have any predictions to offer you about the nature or timing of Congressional action, but that might be just as well because last month I confidently predicted the Philadelphia Phillies would sweep the Orioles in four straight games. Over the years, I have found that predicting the outcome of the World Series is much easier than calling the outcome of legislation in the Congress of the United States.

The first question we ought to look at is "Why should the Clean Air Act be reauthorized?"

The answer is that the Congress intended it that way.

Many of the basic authorities have expired. When the Congress enacted the 1977 amendments, it obviously envisioned a thorough review of the Act, an updating if you will, a tightening where necessary, a relaxation where appropriate. Some of the major innovations of the 1977 amendments were just that: new, untried, even experimental. Clearly the Congress intended those programs to be modified, refined or even discarded on the evidence of how they worked in practice. To aid the Congress, the Administration and the public in the making of judgments about mid-course corrections, the

Congress created the National Commission on Air Quality and mandated a report from that Commission by March 1, 1981. Incidentally, the language of the statute was very specific: The Commission would cease to exist on March 1, 1981, including payment of salaries and expenses, if it failed to file its report on that day, but if the filing took place successfully, the Commission had until May 1, 1981, to wind up its work. Needless to say, the Commission successfully met its deadline, and its payroll, that week.

So the Congress, legislating in the '70's but knowing that the Act had to carry our country through the 1990's and into the 21st century, quite prudently in my judgment called for a reauthorization of the Act's basic authorities in 1981 and thus built into the Act a requirement that a future Congress look at the same problems again, armed with the experience earned in the field, from the vantage point of a new and different present. The Congress, it seems to me, was acknowledging that things change.

Let me reinforce that with some examples: When the Clean Air Act Amendments became law in December 1970, Persian Gulf crude oil was selling at $2.50 a barrel, FOB Abu Dhabi.

The Shah was laying plans for the celebration of the 2,000th anniversary of Iran.

The prime rate was under 6 percent.

The total Federal budget for FY '71 was $210 billion with a staggering deficit of $21.9 billion.

President Nixon was thinking about setting up a committee to run his reelection campaign for 1972.

The Watergate was a hotel.

And a fellow named William Doyle Ruckelhaus was about to be sworn in as Administrator of a brand new outfit called EPA.

It's a changing world we live in.

But back to the Congressional intent: there was another reason why the Congress was so adamant about the timely filing of the report of the National Commission and that had to do with another deadline contained in the '77 Amendments. The 1970 Amendments to the Clean Air Act originally called for the attainment of national ambient air quality standards in all jurisdictions by 1975, although EPA could grant extensions until 1977.

The 1977 Amendments extended the ambient air quality attainment dates to 1982, but with respect to the transportation related pollutants, ozone and carbon monoxide, EPA was authorized to push attainment dates beyond 1982, as far out as 1987.

But there was a catch, as you know: Congress added a system of area-specific, pollutant-specific, construction prohibitions. To receive an extension to 1987, however, state plans had to satisfy what we call Part D requirements, including the adoption of motor vehicle inspection and maintenance program and transportation control measures.

If a state failed to submit an approvable Part D plan for a nonattainment area, the law prohibited further construction in that area of new or modified major sources that emit a pollutant for which the area is in nonattainment. And if transportation control measures are required, and if the Governor has neither submitted a plan nor made a reasonable effort toward devising one, DOT is required to withhold grants for highway construction and EPA may even withhold sewage treatment grants. The construction moratorium is now in effect in over a third of the states and the highway grant cutoff is in effect in two counties in Kentucky.

Our basic concern with the nonattainment scheme in the '77 Amendments is that we know all areas will not meet the national standards, even by 1987. We know that certain areas will not meet the ozone standard regardless of what reasonable measures they take, regardless of what controls they impose, between now and then. Congress therefore will have to address the problem of attainment deadlines in the Clean Air Act Reauthorization.

If nonattainment Part D is complex, Prevention of Significant Deterioration, Part C of the '77 Amendments is downright mysterious. Walter Barber once told a Congressional Committee that "few people in or out of government fully understand . . ." the program and no one rose to dispute his finding.

It is probably impossible to write the history of PSD in less than 100,000 words. It was originally the subject of a Sierra Club lawsuit dating from 1971 against William D. Ruckelshaus in his first incarnation, based on the idea of protecting air quality in pristine regions, an idea which unfortunately had no statutory language on which to rest in the 1970 Amendments. The Federal District Court granted Sierra Club's request for an injunction to force EPA to mount such a program, but it wrote no opinion, hence offered no guidance. The Court of Appeals affirmed the injunction, again without opinion. The United States Supreme Court affirmed by dividing evenly, 4 to 4, but again the Court offered no opinion. EPA bravely came up with a regulatory scheme in 1975, which the Congress ultimately approved by incorporating it bodily into the '77 Amendments. EPA then put out new regulations which were immediately challenged, and the Court of Appeals overturned them in part and affirmed them in part in the Alabama Power case. So the pattern is: the suit; the regs; the law; the regs; the suit and then the current regs.

Nobody I know argues about the propriety of protecting, in a very strenuous way, the pristine air in and around our National Parks - the Class I PSD areas today. Sometimes a source must obtain both a Federal and state permit and occasionally may be subject to both PSD and nonattainment provisions of the '77 Amendments. Sources are frequently required to get extensive and costly field monitoring data which may or may not be useful to the decisionmaker looking at a final decision up or down on a permit.

Incidentally, the National Commission on Air Quality recommended that PSD Class III be eliminated entirely, Class II drastically cut back and that the tracking of short-term increment consumption be terminated. Only Class I would remain intact, if the Commission had its way.

There is logic in making all new source reviews internally consistent, and it seems to me you can still be an advocate of simplification and streamlining this program without being accused of favoring the deterioration of air quality in clean air areas.

When they are at it, Congress may want to do something about SIP's. Even its supporters - and I am one - admit that the process is entirely too complex and too burdensome. The law requires formal Federal approval of the initial State Implementation Plan and most subsequent amendments or adjustments. That requirement taxes EPA's resources in both dollars and people - and in time. EPA must even review SIP revisions calling for specific emission limits for specific industrial plants.

Under the statute, EPA has only four months to take action on a SIP. Needless to say there are delays in processing this mountain of paper.

If we really mean what we say about partnership with the states, we ought to have that reflected in the Act which should entrust the day-to-day management of the air programs to the states or counties, with a strong oversight role for EPA. We shouldn't have to go through formal rule making procedures under the Administrative Procedures Act in approving or disapproving an amendment to a SIP which slightly raises or slightly lowers an emission limit on some factory in some suburb of some city. It also strains our relations with the states at a time when they should be strengthened.

It is also no secret that EPA has trouble with Section 112 of the Act - NESHAPs - National Emissions Standards for Hazardous Air Pollutants. A hazardous air pollutant is defined as one that may be reasonably anticipated to result in an increase in mortality or serious irreversible or incapacitating illness. These are the toxic pollutants which even in small doses can be very dangerous to public health and which can be - and frequently are - carcinogenic. The Administrator is enjoined to set a standard for such a pollutant which provides "an ample margin of safety" to protect the public health.

But we all know there are no absolutely safe levels for some health effects. The absence of a clear threshold for many adverse effects is inconsistent with the concepts of "safe" levels and "ample margins" of safety. It is understandable, I think, that EPA has not acted quickly in listing pollutants under this section. In the Reauthorization, we will be looking for clearer guidance from the Congress about how we can best deal with the problem, given the limits of our scientific knowledge, the limits of our resources - people, money, and time. No one disputes the need to control hazardous air pollutants. The question is not "if" but "how" we should go about it.

Transboundary air pollution is another area of lively interest for all parties in the Reauthorization, particularly since acid rain is on everybody's tongue - and we know that makes for acid tongues.

The problem is that the current statutory authorities most likely to help, don't: Section 115 allows EPA to act on reports from an international agency to determine if air pollutants emitted in the United States cause or contribute to pollution which endangers public health in another country. To trigger Section 115, the foreign country must provide for reciprocal statutory authorities. EPA can then require the state in which the pollution originates to take action to correct the problem.

Section 126 deals with interstate pollution. An aggrieved state - that is, a state which believes that emissions from another state upwind are preventing it from achieving or maintaining standards - the State on the receiving end of the pollution may petition EPA to limit such emissions in the state where they originate.

Our problem with both 115 and 126 is to make a causal link between a specific source giving off emissions somewhere and the pollution that occurs hundreds, or even thousands, of miles away from that source. Our limited understanding of long-range transport, atmospheric chemical transformations, imprecise models all come together to prevent us from making the causal connections the Act requires before remedial action can occur. This is one of the areas the Congress will have to look at, regardless of what approach it ultimately takes on acid rain.

There are a dozen other areas of the Act that the Congress will look at in its reauthorization process - big issues in the mobile source area for instance: auto emissions, particularly $NO_x$, high altitude emissions, diesel particulates, heavy duty truck standards. There are tough issues in stationary sources, as the members of this symposium know very well - visibility protection, percentage reduction, noncompliance penalties, and NSR and RACT, LAER and BACT, etc.

This litany of problems, however, should not obscure the fact that the Clean Air Act has worked.

It may be one of the most complex pieces of legislation ever devised by the hand or mind of Congress. It may be at times unwieldy, at times inflexible, now and then even cantankerous, but it works. The air is measurably cleaner around our country because it works. The public health is better served now than it was before the Act became law in 1970.

The recitation of the difficulties we have with the Act is not, I hope, understood as totally negative criticism. On the contrary, it is offered with a positive goal in mind: we want to see something that is good, made better. We want to see the Act made more effective by discarding some of the duplications and red tape that slow us down now. We want the Act to be flexible enough to carry us through the '80's and 90's into the next century. We want to get the burdensome requirements eased and the nonessential elements deleted completely. We don't want to see economic growth and development stymied in our country by requirements that have little to do with assuring clean air.

The issues are tough because our society is so complex, so varied, so diverse. But that is also one of our great strengths, and one of the reasons why far-reaching statutes like the Clean Air Act are, almost by definition, controversial: they deal with so many interests, cut across so many industries, involve such great social and economic costs and generate such a wide range of conflicting claims and counterclaims.

I said at the beginning that I hoped to shed some light on why the Reauthorization was so difficult and so time consuming, and identify some basic elements that any proper reauthorization had to take into account. I hope I have done that.

I thank you for your kind attention.

# THE RESOURCE CONSERVATION AND RECOVERY ACT: CURRENT AND PROJECTED REGULATIONS

by

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(Abstract and paper were not submitted)

# TRENDS IN COMMERCIAL APPLICATIONS OF FGD

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November 1, 1983
Opening Session

## ABSTRACT

PEDCo Environmental, Inc., has been monitoring and reporting on the status of utility flue gas desulfurization (FGD) technology since 1974. During the period of 1974 to 1982, this effort was supported by the U.S. Environmental Protection Agency (EPA) under the direction of the Industrial Environmental Research Laboratory - Research Triangle Park. Starting this year, this effort is now jointly sponsored by EPA and the Electric Power Research Institute (EPRI). Project direction from EPRI is provided by the Coal Combustion Systems Division.

Information for this program is obtained by visits to plants having operational FGD systems and through regular contacts with the owner/operator utilities who are presently operating or planning FGD installations. Supplemental information is also solicited from FGD system and equipment suppliers, design/engineering firms, research organizations, and regulatory agencies.

The information collected in this program is stored in the Flue Gas Desulfurization Information System (FGDIS), which is a collection of computerized data base files containing descriptive, design, performance, and cost data for all the FGD systems identified in FGDIS. FGDIS has the dual capability of generating the periodic survey report (now available through EPRI) as well as permitting immediate access to the data files via remote terminal. This latter feature allows private and government users to access directly FGDIS at any time in order to conduct custom-designed data analyses, examine detailed data that may be too specific to be conveniently included in the survey report, or review information that has been loaded into the system but not yet published in the quarterly report.

This paper summarizes the status of FGD technology as of June 1983 and highlights the status of the electric utility power industry and projected growth of coal-fired power generation, the present status and future trends in the growth of FGD, developments in system design and application, current operating experience, and costs.

As of June 1983, there were 114 FGD systems in service representing 45,750 MW (gross) of equivalent power generating capacity. Another 100 systems representing 59,324 MW were under construction and planned. Approximately 16 percent of the present coal-fired generating capacity is controlled by FGD. This figure is projected to rise to 34 percent during the next 10 years.

# NOTES

1. Company Names and Products.

   The mention of company names or products is not to be considered an endorsement or recommendation for use by the U.S. Environmental Protection Agency.

2. Consistency of Information.

   The information presented was obtained from a variety of sources including the owner/operator utilities, FGD system and equipment suppliers, design/engineering firms, research organizations, and regulatory agencies. The information was acquired through a variety of methods including plant visits, telephone contacts, written communications, and other technical reports. Accordingly, the consistency of information on a particular system and between the several systems discussed may be lacking. The information presented is basically that which was voluntarily submitted by users and developers with some interpretation by the authors. The order of presentation of information or the amount of information presented for any one system should not be construed to favor or disfavor that particular system.

3. Units of Measure.

   EPA policy is to express all measurements in metric units. When implementing this practice will result in undue cost or affect clarity, conversion factors are provided for the non-metric units. This paper uses British units of measure.

   The following equivalents can be used for conversion to the metric system:

| British | Metric |
|---|---|
| 5/9 (°F-32) | °C |
| 1 ft | 0.3048 m |
| 1 $ft^2$ | 0.0929 $m^2$ |
| 1 $ft^3$ | 0.0283 $m^3$ |
| 1 grain | 0.0648 gram |
| 1 lb (avoir.) | 0.4536 kg |
| 1 ton (long) | 1.0160 m tons |
| 1 ton (short) | 0.9072 m tons |
| 1 gal. | 3.7853 liters |
| 1 lb/$10^6$ Btu | 429.6 ng/J |
| 1 Btu/kWh | 1055.056 J/kWh |

# PROGRAM OVERVIEW

For approximately 10 years, PEDCo Environmental has monitored and reported on the development and growth of flue gas desulfurization (FGD)* technology for utility fossil-fuel-fired boilers in the United States. From 1974 to 1982, this program was solely supported by the U.S. Environmental Protection Agency (EPA) under the direction of the Industrial Environmental Research Laboratory-Research Triangle Park. In 1983, this program was continued under a joint sponsorship agreement between EPA and the Electric Power Research Institute (EPRI). Project direction within EPRI is provided by the Coal Combustion Systems Division.

The overall objective of the program still remains the same: to provide an objective and current perspective of FGD technology as applied to utility fossil-fuel-fired boilers and facilitate, through information dissemination, improvements in system design, performance, and costs for present and future facilities.

Utilities, system and equipment suppliers, design/engineering firms, research organizations, regulatory agencies, and others all volunteer the information for this program. This voluntary approach facilitates timely dissemination of pertinent information in this key technological area.

All information gathered for this program is housed in a computerized data base called the Flue Gas Desulfurization Information System (FGDIS). Design and performance data for both the operational and planned domestic utility FGD systems are stored in FGDIS. Also stored are data on operational domestic scrubbers for removal of particulate matter and data on operational FGD systems applied to coal-fired utility boilers in Japan.

The design data fields contained in FGDIS encompass the entire emission control system and the power-generating unit to which it is applied. General descriptive data fields include plant location, standards limiting emissions of $SO_2$ and particulate matter, power-generating capacity, boiler and stack information, average fuel analyses, and other more general data. The design data fields assigned for the FGD system range from general information such as process type, system supplier, and initial system start-up date to more specific component design information and operating parameters such as absorber type, gas and liquid flow rates, pressure drop, and materials of construction. Also included in the data are descriptions of the methods of solids concentration and waste disposal, reagent preparation and handling, flue gas reheat, mist elimination, and information on capital costs and annual revenue requirements.

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* FGD refers to post combustion dry or wet processes for $SO_x$ emission control.

For the operational FGD systems, FGDIS stores comprehensive performance data, including periodic dependability parameters and the service times from which they are calculated. Where available, actual $SO_2$ and particulate matter removal efficiencies are included (and qualified). Problems encountered with system operation and the solutions implemented to correct them are coded and described. The performance of the FGD-equipped boiler is described in terms of service time, production level, and capacity factor.

In addition to being used to generate a periodic survey report, FGDIS is also available for direct on-line access. This important function not only provides interested parties with an opportunity to examine data that are too specific for convenient inclusion in the report, but it also provides immediate access to information that has been loaded into the system but not yet published (i.e., information that has become available during the period between reports). Information is gathered, reduced, verified, and loaded into FGDIS on a continual basis to ensure that the files remain current and complete.

Access to the FGDIS data files and management of these data are accomplished via a computer software package known as System 2000® developed by the Intel Corporation. This comprehensive data base management system offers extensive data retrieval capabilities. The set of user-oriented commands provided are flexible enough to satisfy virtually any information need. Utilization of system functions (average, standard deviation, summation, maximum value, and minimum value) can be used to analyze the numerical data contained in the files. In addition, the data requested through the available commands can be selectively limited by a set of criteria included in the commands. This feature facilitates examination of design or performance parameters for a specific unit or a specific process type, and so on. The retrieval and analytical possibilities are limited only by the needs and imagination of the user.

The FGDIS files are stored at EPA's National Computer Center (NCC) in Research Triangle Park, North Carolina.

# TECHNOLOGY OVERVIEW

## CURRENT STATUS

### United States Electric Utility Power Industry[1,2]

The generating capacity of the electric utility power industry in the United States can be examined in two ways: installed capacity and production capacity. Installed capacity represents the full-load continuous rating of a unit as installed, irrespective of how it is operated. Production capacity represents the generating output of a unit for a period of time, typically a year.

As of the end of 1982, the electric utility power industry in the United States contained a total of 10,818 power-generating units representing a combined installed power-generating capacity of approximately 656 gigawatts (GW). A breakdown of these installed totals by primary energy source is provided in Table 1.

For the period of January to December 1982, the electric utility power industry in the United States produced a total of approximately 2,241,000 gigawatt-hours (GWh). This production level represents an industry capacity factor of 39 percent, based on the maximum attainable output available from the total installed power-generating capacity. A breakdown of the 1982 production level by primary energy source is provided in Table 2.

As indicated in Tables 1 and 2, coal-fired power generation accounts for 1347 units and approximately 278 GW of installed capacity and approximately 1,188,000 GWh of production capacity. It is noteworthy that although coal represents approximately 42 percent of the installed capacity, it accounts for approximately 53 percent of the production capacity.

The coal-fired capacities represented in Tables 1 and 2 can also be regarded in terms of fuel consumption. The 1982 production capacity represents approximately 636 million tons of coal consumption.

### United States Electric Utility Flue Gas Desulfurization

The status of FGD technology as applied to coal-fired utility boilers in the United States is presented in Table 3. This table summarizes the number and installed capacity of FGD-equipped units in service, under construction, and firm planning as of June 1983.

## TABLE 1. STATUS OF INSTALLED CAPACITY OF UNITED STATES ELECTRIC UTILITY POWER INDUSTRY AS OF DECEMBER 1982

| Primary energy source | Installed capacity, MW | No. |
|---|---|---|
| Coal | 278,159 | 1,347 |
| Oil | 151,377 | 4,399 |
| Gas | 75,320 | 1,640 |
| Nuclear | 68,963 | 84 |
| Hydro | 78,843 | 3,291 |
| Other | 3,696 | 57 |
| Total | 656,358 | 10,818 |

## TABLE 2. STATUS OF PRODUCTION CAPACITY OF UNITED STATES ELECTRIC UTILITY POWER INDUSTRY FOR JANUARY-DECEMBER 1982

| Primary energy source | Production capacity, GWh |
|---|---|
| Coal | 1,187,842 |
| Oil | 134,473 |
| Gas | 313,770 |
| Nuclear | 291,356 |
| Hydro | 313,770 |
| Total | 2,241,211 |

TABLE 3. NUMBER AND INSTALLED CAPACITY OF UTILITY FGD SYSTEMS

| Status | No. of units | Total controlled capacity, MW[a] | Equivalent scrubbed capacity, MW[b] |
|---|---|---|---|
| Operational | 114 | 45,750 | 42,135 |
| Under construction | 27 | 14,712 | 14,441 |
| Planned: | | | |
| Contract awarded | 18 | 11,494 | 11,386 |
| Letter of intent | 7 | 6,060 | 6,060 |
| Requesting/evaluating bids | 6 | 3,400 | 3,400 |
| Considering only FGD systems | 42 | 23,658 | 23,480 |
| TOTAL | 214 | 105,074 | 100,902 |

[a] Summation of the gross unit capacities (MW) brought into compliance by the use of FGD systems regardless of the percentage of the flue gas scrubbed by the FGD system(s).

[b] Summation of the effective scrubbed flue gas in equivalent MW, based on the percentage of flue gas scrubbed by the FGD system(s).

As indicated in Table 3, there are 114 FGD-equipped units in service representing an installed generating capacity of 45,750 MW (gross). Comparing these figures with the figures presented in Table 1 for coal-fired power generation reveal that approximately 8 percent of the units and approximately 16 percent of the installed capacity are equipped with FGD systems. Moreover, if production capacity is analyzed, it appears that FGD-equipped units account for approximately 241,000 GWh of production which, when compared with that for coal-fired power generation (Table 2), represents approximately 20 percent of the overall production level for 1982.

## GROWTH TRENDS[1,6]

FGD technology has been available for service on utility boiler flue gas for approximately 50 years. The most significant period of development has occurred since 1966 when limestone injection/tail-end wet scrubbing was first introduced in the United States and tested on coal-fired boiler flue gas. Since that time, there have been more than 125 FGD systems operated on utility boilers, primarily as commercial facilities and secondarily as experimental prototype or demonstrational facilities.

A comparison of coal-fired power generation with FGD-equipped coal-fired power generation with respect to projected growth reveals a number of interesting trends.

If growth of the installed capacity of coal-fired power generation is compared with FGD-equipped installed capacity during the next 10 years, the relationship illustrated in Figure 1 is observed. Coal-fired power generation is expected to post a net gain of 121 units and approximately 69,500 MW.* This represents an increase of 9 and 25 percent for the number of units and installed capacity, respectively. The net increase for FGD-equipped power generation during the same period is projected at 132 units and approximately 73,250 MW of installed capacity, representing an overall growth of 115 and 160 percent, respectively. The FGD-equipped growth rate slightly exceeds the coal-fired growth rate. This occurs because the FGD-equipped population generally comprises newer units and therefore sees a lower rate of unit retirement than that for the entirety of the coal-fired population. Also, FGD installed capacity will represent approximately 34 percent of the total installed coal-fired capacity in place in 10 years, up from approximately 16 percent at present, based on plans submitted by the utility industry.

If the growth of coal consumption is analyzed, projected changes in fossil fuel requirements for utility power generation for the next 10 years show coal use expanding by approximately 36 percent - from 636 million tons to 862 million tons.

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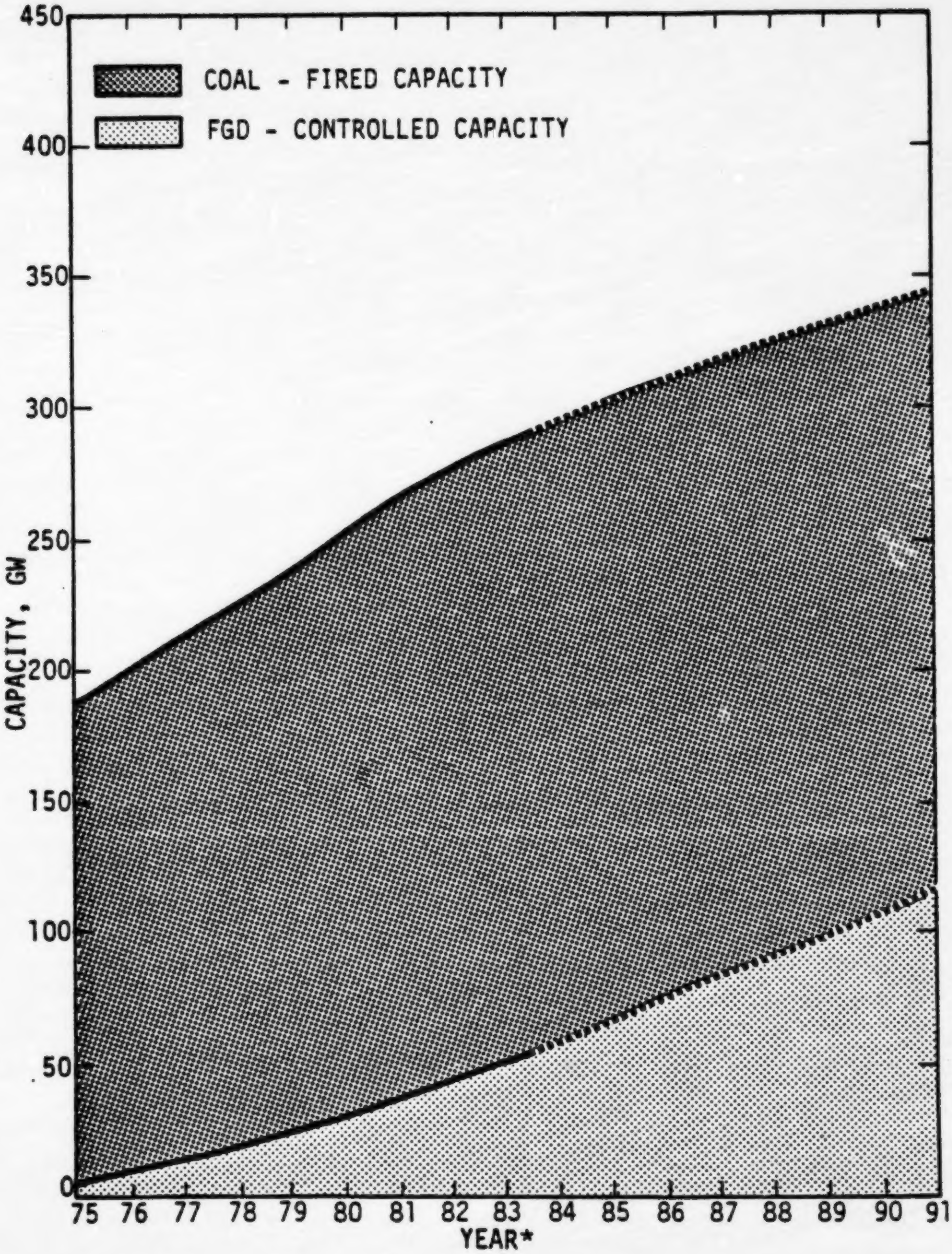
* Net gain accounts for the retirement of older units.



* YEAR-END TOTALS

Figure 1. Growth of coal-fired installed capacity and FGD installed capacity from 1975 through 1991.[1-6]

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If the growth of FGD is examined in and of itself, a number of interesting trends are evident regarding year of projection, utility experience, and system supplier experience.

With respect to year of projection, a historical review of the annual status of FGD technology in the utility industry is illustrated in Figure 2. This figure displays the operating, under construction, and planned installed capacities which existed at year's end for the period of 1970 to mid-1983. This figure reflects a significant growth in operating capacity since 1972. A rise is also noted in the capacity under construction from 1970 to 1977 and a fairly stable growth pattern thereafter. Planned capacity also exhibits significant growth through 1980; however, it sharply declines thereafter.

With respect to utility experience, 66 separate utility companies have direct experience in operating FGD systems. Moreover, many of these companies have multiple system experience (32), or single system experience with additional system(s) under construction or planned (25). A number of utility companies are constructing or planning FGD systems with no previous operating experience (28).

The significant growth in utility FGD experience can also be analyzed by quantifying the number of FGD hours accumulated by each utility for its respective system(s). The utility companies with significant experience levels are listed in Figure 3. The hours listed represent aggregate elapsed calendar time, from system(s) start-up to the present (mid-1983). Actual service or dependability considerations are not factored into this analysis for a variety of reasons. First, we are presenting a simplistic means by which to compare relative utility experience levels in FGD. Second, regardless of the dependability or service requirements associated with a given FGD system, the utility will continue to accumulate experience with it.

A similar analysis can also be performed for the system suppliers. The results of this analysis are presented in Figure 4. The suppliers listed in Figure 4 represent those companies who have provided commercial FGD systems and are currently active in the commercial market. Again, the experience hours listed represent aggregate elapsed calendar time for their respective systems, irrespective of actual service or system dependability considerations.

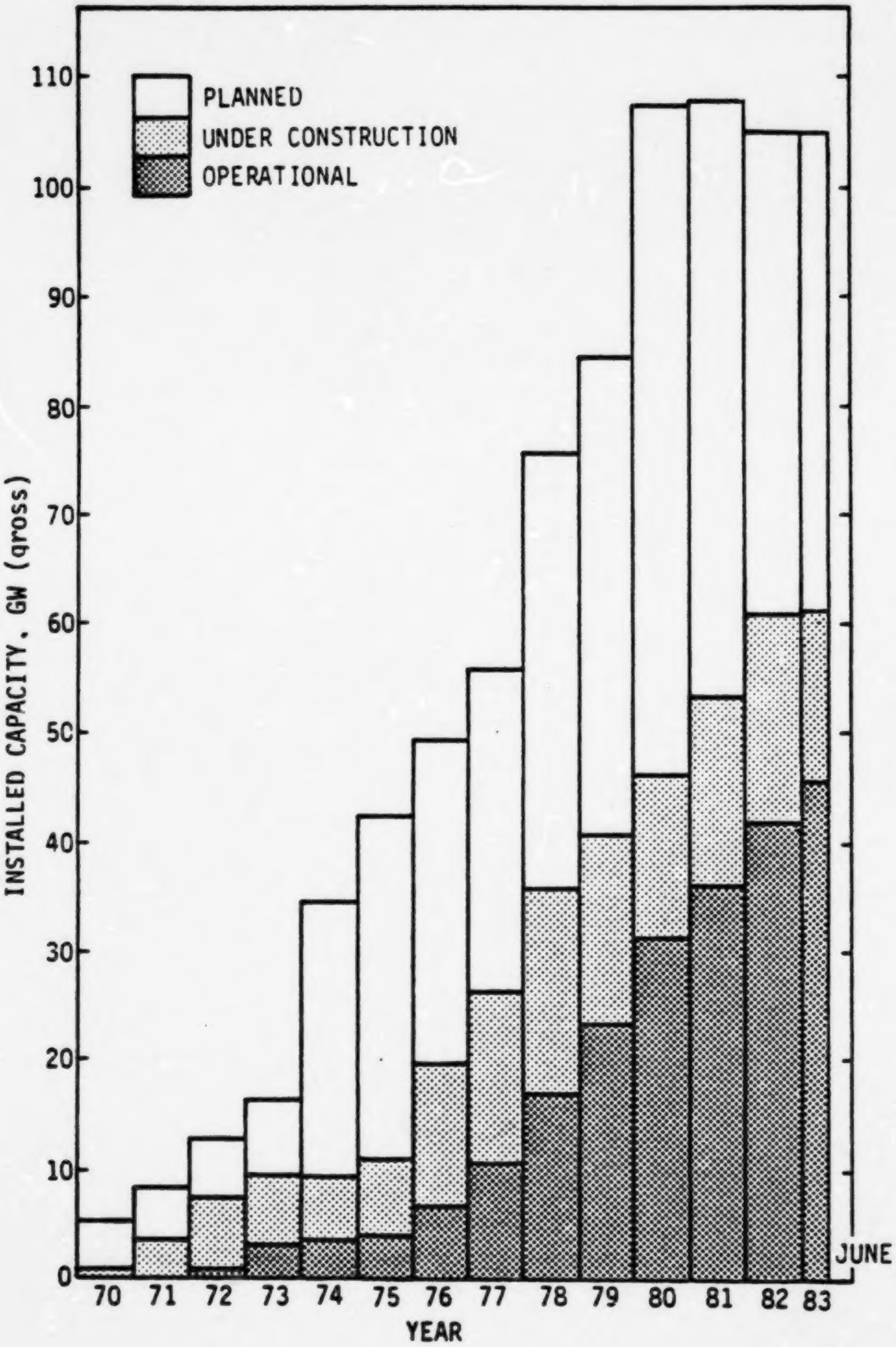

Figure 2. Historic review of the annual status of utility FGD.

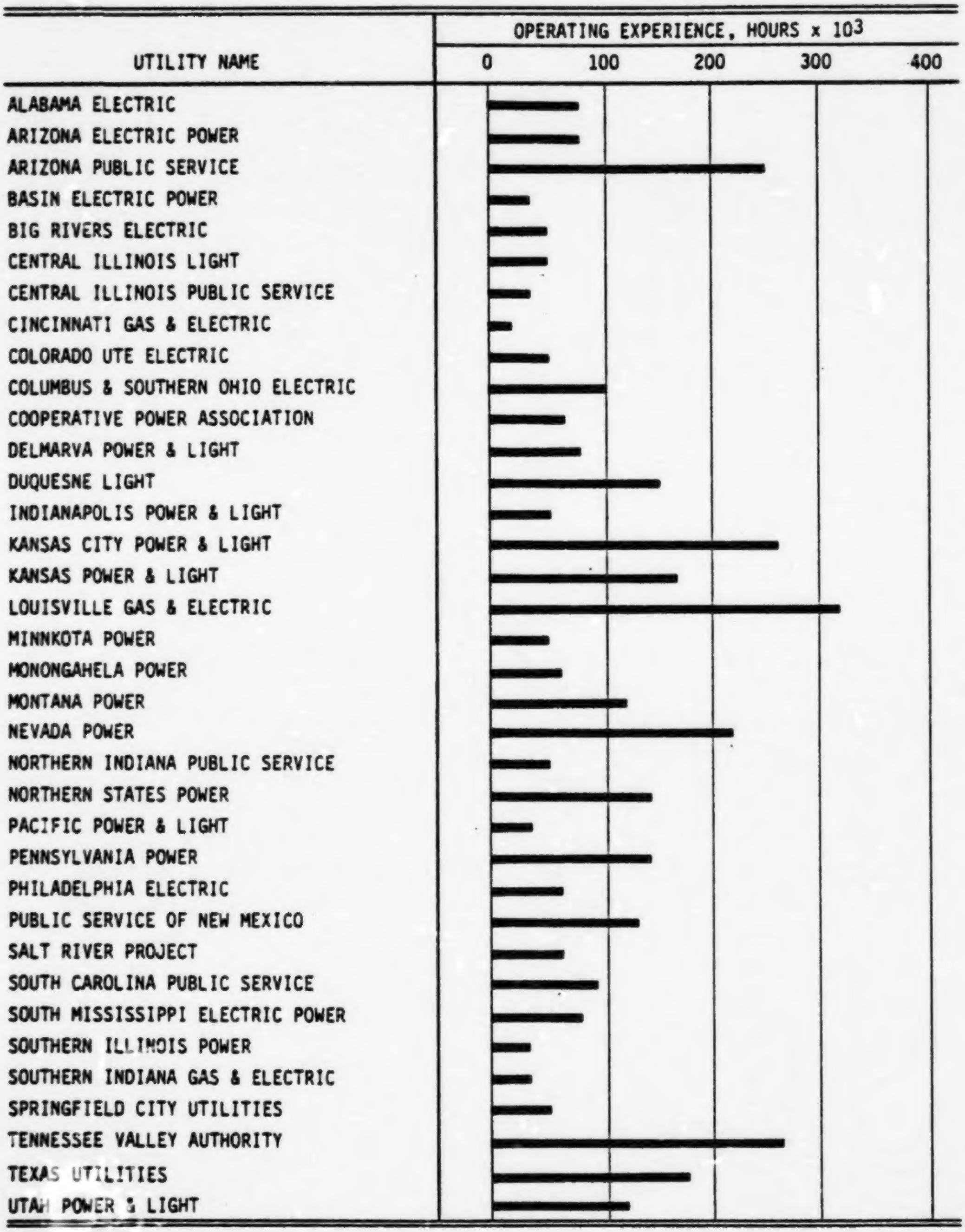

Figure 3. Utility company FGD operating experience.

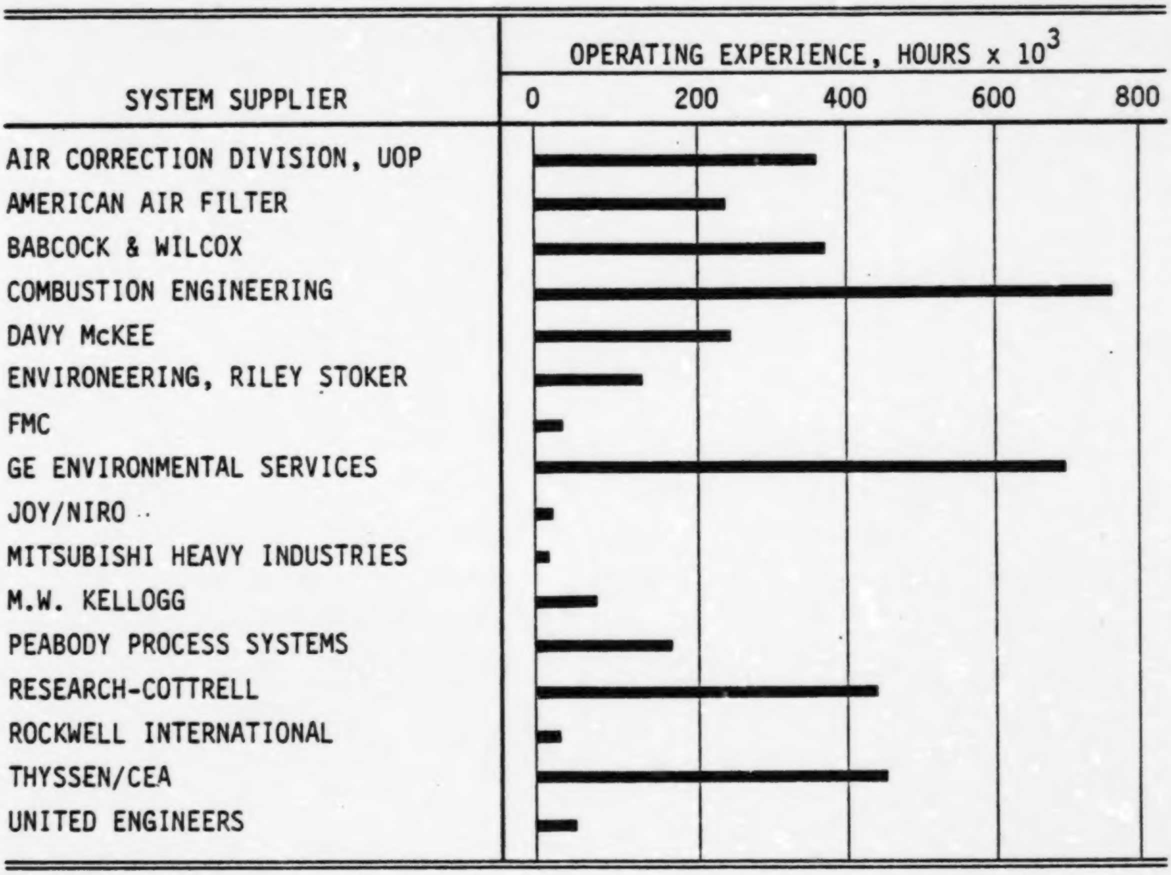

Figure 4. FGD operating experience associated with system suppliers.

# DEVELOPMENTS IN SYSTEM DESIGN AND APPLICATION

A number of significant developments have affected the electric utility power industry in the United States with respect to the application and design of FGD systems for coal-fired power generation. These developments include revised (and more stringent) air emission control standards, decline in power demand, increases in new plant lead time and costs, and the supply and costs of fossil fuels. These developments have affected the selection of emission control strategies, FGD processes, and FGD system design configuration.

## EMISSION CONTROL STANDARDS

The current environmental driving force for $SO_2$ emission reduction is the Clean Air Act, implemented in 1970 and amended in 1977, which created a schedule to decrease $SO_2$ emissions from power plants and other major sources for both new and existing facilities. New sources are regulated by the New Source Performance Standard (NSPS) of December 1971 and the current or revised NSPS of June 1979. In addition, the Clean Air Act amendments indirectly provide for regulation of existing power plants because State Implementation Plans (SIPs), required for each state, include a control strategy for ensuring maintenance of the promulgated ambient air quality standards for $SO_2$ and other regulated pollutants.

The FGD-equipped units identified in FGDIS are classified according to one of five basic regulatory classification categories. These categories are identified in Table 4 complete with a summary of the number of units and installed capacities by status.

## EMISSION CONTROL STRATEGIES

The control of particulate matter must be considered along with the installation of an FGD system. The three basic methods currently considered are electrostatic precipitation, fabric filtration, and wet scrubbing. There are a number of site and design factors involved in such a selection process as they relate to FGD:

- Dry collection of fly ash upstream may be desirable for use as an additive to fix or stabilize the waste.

## TABLE 4. FGD SYSTEMS BY STATUS AND REGULATORY CLASSIFICATION

| Regulatory classification | Operational |  | Under construction |  | Planned |  | Total |  |
|---|---|---|---|---|---|---|---|---|
|  | No. | MW | No. | MW | No. | MW | No. | MW |
| More stringent than 6/79 NSPS | 12 | 5,394 | 14 | 7,899 | 27 | 15,706 | 53 | 28,999 |
| 6/79 NSPS | 9 | 2,746 | 7 | 3,809 | 42 | 26,886 | 58 | 33,441 |
| Less stringent than 6/79 NSPS and more stringent than 12/71 NSPS | 40 | 17,967 | 2 | 1,151 | 3 | 1,650 | 45 | 20,768 |
| 12/71 NSPS | 41 | 16,912 | 4 | 1,853 | 1 | 370 | 46 | 19,135 |
| Less stringent than 12/71 NSPS | 12 | 2,731 | - | - | - | - | 12 | 2,731 |
| Total | 114 | 45,750 | 27 | 14,712 | 73 | 44,612 | 214 | 105,074 |

- Dry collection upstream decreases the solids loading on the FGD system which can create or promote plugging, scaling, or erosion of internals.

- The fly ash may contain alkaline compounds that assist in $SO_2$ removal in the combined scrubbing of fly ash and $SO_2$.

- Plants faced with the necessity of retrofitting an FGD system may contain existing fly ash collection equipment of marginal performance capability, thus making fly ash and $SO_2$ scrubbing an economically attractive option.

- Supplemental fly ash collection is an inherent design feature of some regenerable/product-recovery technologies for process considerations. Supplemental fly ash removal (as well as absorption of $SO_3$ and HCl) may occur via a separate wet scrubbing step or, less frequently, use of a wet ESP.

- The selection of a dry scrubbing system involves the collection of particulate matter containing $SO_2$ reaction products and fly ash.

- New plants faced with stringent particulate emission regulations may use the FGD wet scrubber to provide secondary particulate removal and thus save on the costs associated with an extremely high efficiency upstream particulate matter collection device.

The methods used and planned for future use on FGD-equipped units are tabulated in Table 5. A clear preference for ESP's is shown. The emergence of fabric filters is driven by the increasingly popular application of dry scrubbing technology. Wet scrubbing for particulate matter control, although significant in currently operational units, shows a clear decline in future FGD-equipped units.

## FGD PROCESS APPLICATION

Application of FGD technology requires the consideration of design characteristics, including the use of waste producing or product recovery technologies, regenerable versus nonregenerable technologies, chemical reagent and additive selection, and coal sulfur content. A brief overview of FGD technology with respect to these factors for systems presently in service and planned for imminent future service is discussed below.

FGD systems currently in service, under construction, and contract awarded are shown in Table 6 as a function of throwaway

TABLE 5. FGD-EQUIPPED PARTICULATE MATTER EMISSION CONTROLS

| | Operational | | Under construction | | Contract awarded | | Total | |
|---|---|---|---|---|---|---|---|---|
| | No. | MW | No. | MW | No. | MW | No. | MW |
| Electrostatic precipitator | 68 | 28,266 | 16 | 9,806 | 15 | 9,544 | 99 | 47,616 |
| Fabric filter | 7 | 1,989 | 8 | 2,802 | 3 | 1,950 | 18 | 6,741 |
| Wet scrubbing | 22 | 8,220 | 2 | 1,400 | - | - | 24 | 9,620 |
| ESP/wet scrubbing (process) | 8 | 2,576 | - | - | - | - | 8 | 2,576 |
| ESP/wet scrubbing (secondary particulate) | 9 | 4,699 | 1 | 704 | - | - | 10 | 5,403 |
| Total | 114 | 45,750 | 27 | 14,712 | 18 | 11,494 | 159 | 71,956 |

## TABLE 6. SUMMARY OF FGD PROCESS DESIGN

| | Operational | | Under construction | | Contract awarded | | Total | |
|---|---|---|---|---|---|---|---|---|
| | No. | MW* | No. | MW* | No. | MW* | No. | MW* |
| Throwaway product | | | | | | | | |
| Wet | | | | | | | | |
| Nonregenerable | | | | | | | | |
| Limestone | 51 | 20,756 | 13 | 7,546 | 11 | 7,591 | 75 | 35,893 |
| Lime | 34 | 13,634 | 5 | 3,350 | 2 | 1,090 | 41 | 18,074 |
| Sodium carbonate | 6 | 1,505 | - | - | - | - | 6 | 1,505 |
| Regenerable | | | | | | | | |
| Dual alkali | 4 | 1,572 | 1 | 391 | 1 | 265 | 6 | 2,228 |
| Dry (nonregenerable) | | | | | | | | |
| Lime | 5 | 1,214 | 7 | 2,679 | 4 | 2,440 | 16 | 6,333 |
| Sodium carbonate | 1 | 440 | - | - | - | - | 1 | 440 |
| Salable product | | | | | | | | |
| Wet | | | | | | | | |
| Nonregenerable | | | | | | | | |
| Limestone | 1 | 166 | 1 | 475 | - | - | 2 | 641 |
| Lime | 1 | 65 | - | - | - | - | 1 | 65 |
| Regenerable | | | | | | | | |
| Wellman Lord | 7 | 1,959 | - | - | - | - | 7 | 1,959 |
| Magnesium oxide | 3 | 724 | - | - | - | - | 3 | 724 |
| Dry (regenerable) | | | | | | | | |
| Aqueous carbonate | 1 | 100 | - | - | - | - | 1 | 100 |
| TOTAL THROWAWAY PRODUCT | 101 | 39,121 | 26 | 13,966 | 18 | 11,386 | 145 | 64,473 |
| TOTAL SALABLE PRODUCT | 13 | 3,014 | 1 | 475 | - | - | 14 | 3,489 |
| TOTAL WET | 107 | 40,381 | 20 | 11,762 | 14 | 8,946 | 141 | 61,089 |
| TOTAL DRY | 7 | 1,754 | 7 | 2,679 | 4 | 2,440 | 18 | 6,873 |
| TOTAL NONREGENERABLE | 99 | 37,780 | 26 | 14,050 | 17 | 11,121 | 142 | 62,951 |
| TOTAL REGENERABLE | 15 | 4,355 | 1 | 391 | 1 | 265 | 17 | 5,011 |

*Equivalent scrubbed capacity

product versus salable product, regenerable versus nonregenerable, wet versus dry, and chemical reagent.

Table 6 reflects a strong industry preference for nonregenerable, calcium-based, wet slurry processes that produce a waste product for disposal. Examining the lime and limestone categories reveals a continuing preference for limestone. The emergence of dry scrubbing technology is reflected in the under construction and planned categories.

The application of FGD systems with respect to coal sulfur content can be analyzed by distinguishing three sulfur ranges:

- Low sulfur coal: less than or equal to 1 percent sulfur in the coal
- Medium sulfur coal: greater than 1 percent but less than or equal to 3 percent sulfur in the coal
- High sulfur coal: greater than 3 percent sulfur in the coal

In accordance with these categories, Table 7 provides a breakdown of FGD systems by coal sulfur content. It is evident from this table that about 50 percent of the FGD systems in each status category are low-sulfur coal applications.

TABLE 7. FGD SYSTEMS BY COAL SULFUR CONTENT

| | Operational | | Under construction | | Contract awarded | | Total | |
|---|---|---|---|---|---|---|---|---|
| Coal sulfur | No. | MW | No. | MW | No. | MW | No. | MW |
| Low | 53 | 22,557 | 15 | 7,727 | 10 | 7,100 | 78 | 37,384 |
| Medium | 26 | 8,663 | 7 | 4,445 | 5 | 2,981 | 38 | 16,089 |
| High | 35 | 14,530 | 5 | 2,540 | 3 | 1,413 | 43 | 18,483 |
| Total | 114 | 45,750 | 27 | 14,712 | 18 | 11,494 | 159 | 71,956 |

# PERFORMANCE OVERVIEW

During the past several years, FGD has become the most commercially developed means of controlling $SO_2$ emissions from coal-fired boilers. FGD operating experience increases each year as more and more systems are placed in service. The FGD survey program has been monitoring the performance of the operating FGD systems and logging monthly operating parameters (e.g., boiler and FGD system operating hours, forced outage times, and scheduled outage times). With this operational information, system performance trends over the years can be analyzed and reviewed.

One important criterion for the evaluation of FGD performance is system dependability. We have developed a number of dependability parameters to measure this index for various situations, conditions, and information-reporting formats. Of these parameters, "availability" seems to be most universally accepted and understood. In context of FGD, system availability is defined as the hours the FGD system is available for operation (whether operated or not) divided by hours in the period. Period hours usually equal hours in a month.

Availability data for operating FGD systems have been collected through the Utility FGD Survey program on a monthly basis. The monthly data were used to calculate the average annual availabilities for each system.

Figures 5 and 6 are the median analyses of the annual average availabilities for all FGD systems (for which data are available); broken down for low-, medium-, and high-sulfur coals.* Median analyses were based on data from the period of 1978 through 1982 (5-year period). In each case, the availability points were plotted and the median was determined.

As can be seen from these figures, low sulfur systems show the steadiest median of the three, with the median changing only a few percentage points. The high sulfur systems exhibit the most dramatic improvement over the period, as well as exhibiting a relatively constant trend for the past 3 years. The medium sulfur coal systems also exhibit significant improvement; however, two fluctuations are observed for 1980 and 1982.

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* The coal sulfur content ranges are defined as less than 1 percent, 1 through 3 percent, and greater than 3 percent for low, medium, and high, respectively.

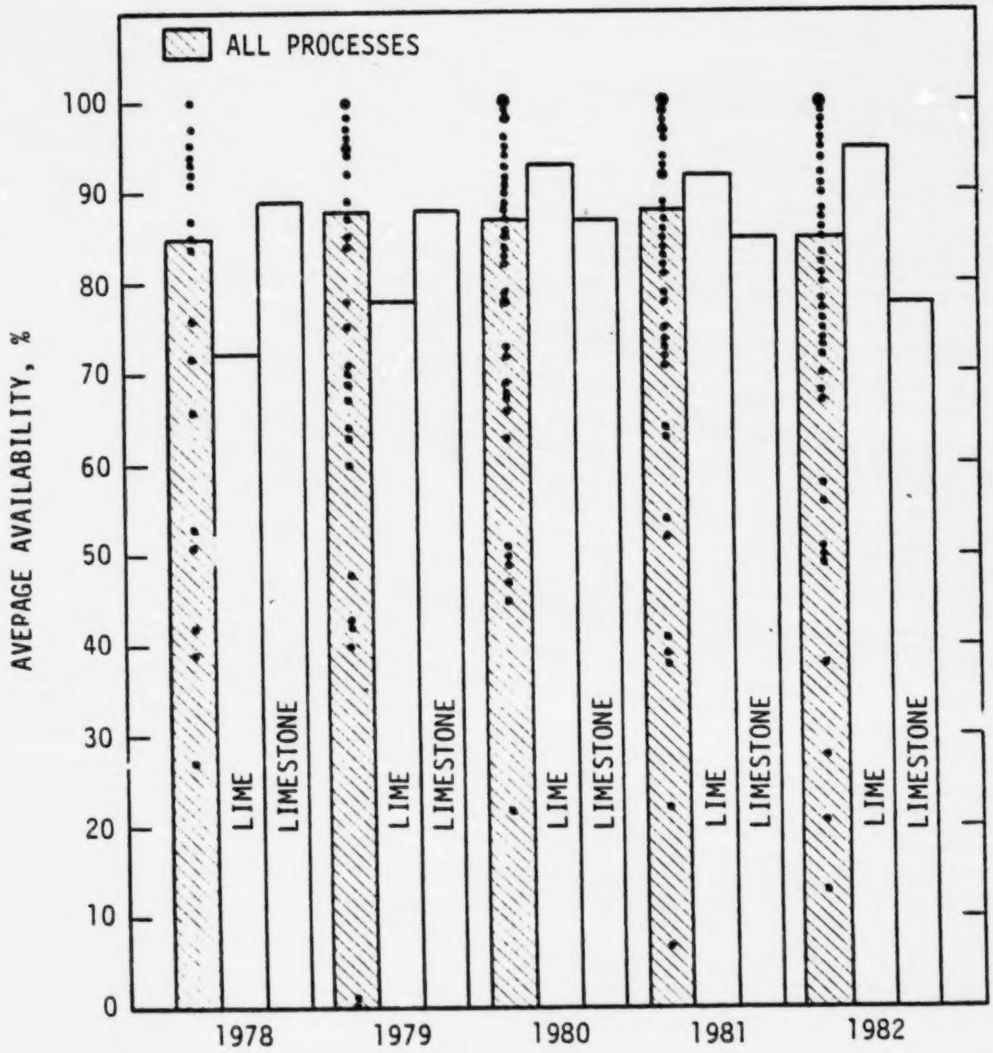

Figure 5. Median analysis of the annual availability for coal-fired FGD systems.[7]

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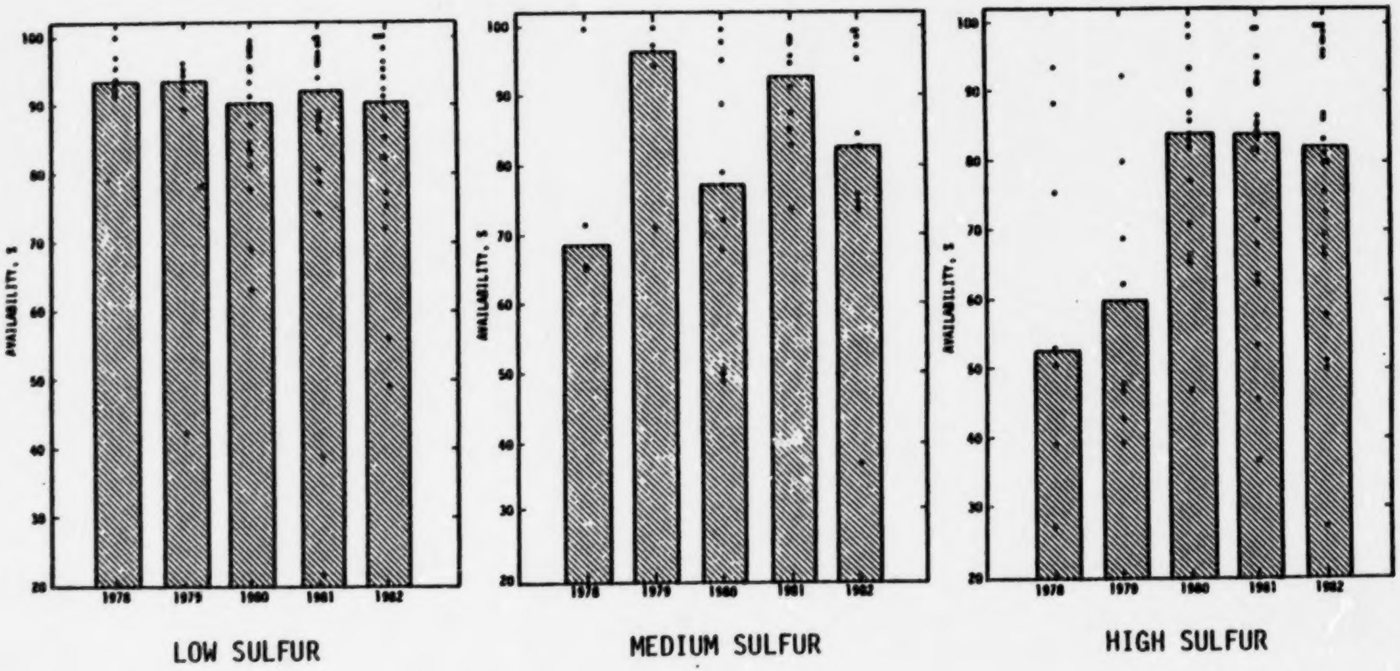

Figure 6. Median availability analysis by coal sulfur content.

Overall, the performance of FGD with respect to system availability tends to show steady improvement. Lime and dual alkali processes have significantly improved the technology's performance on high-sulfur coal.

## COSTS OVERVIEW

Capital and annual cost data for operational FGD systems have been obtained continuously under the utility survey program since March 1978. Costs for each system are obtained directly from the utilities and then itemized by individual FGD cost element. The itemized costs are then adjusted to a common basis to enhance comparability. This adjustment is made by using factors for estimating costs not given by the utilities and by using cost index factors to express all costs in constant year dollars (mid-1981). All adjusted cost data and computations are reviewed and verified with the appropriate utility before publication.

The cost adjustment procedure is summarized below.

### Capital Costs

- All costs associated with control of particulate matter emissions are excluded.
- Capital costs for modifications necessitated by installation of an FGD system are added if they were not included in the reported costs.
- Sludge disposal costs are adjusted to reflect a 20-year life span for retrofit systems and a 30-year life span for new systems.
- Any unreported direct and indirect costs incurred are estimated and included.
- All capital costs are expressed in mid-1981 dollars.
- All capital costs reflect the gross generating capacity of the unit.

### Annual Costs

- Direct costs that were not reported are estimated and added.
- Overhead and fixed costs that were not reported are estimated and added.

- All annual costs are expressed in mid-1981 dollars.
- All annual costs are based on a 65 percent capacity factor and the net generating capacity of the unit.

Table 8 summarizes both reported and adjusted costs for all operational FGD systems on which cost data were obtained. This table also summarizes the results, by application and by process category. Table 9 lists the results by process type. Table 10 provides a plant-by-plant listing of the reported and adjusted costs for the operational FGD systems addressed in this study.

The capital and annual costs for a significant portion of the commercial population reflect an overall cost of approximately $119/kW and 8 mills/kWh, respectively. These figures apply to a wide variety of systems that represent different processes, dates of installation, applications, and severity of duty for units in commercial service from 1972 to 1981.

TABLE 8. CATEGORICAL RESULTS OF THE REPORTED AND ADJUSTED CAPITAL AND ANNUAL COSTS FOR OPERATIONAL FGD SYSTEMS

| | Reported | | | | Adjusted | | | |
|---|---|---|---|---|---|---|---|---|
| | Capital | | Annual | | Capital | | Annual | |
| | Range, $/kW | Average, $/kW | Range, mills/kWh | Average, mills/kWh | Range, $/kW | Average, $/kW | Range, mills/kWh | Average, mills/kWh |
| All | 23.7-213.6 | 80.2 | 0.1-13.0 | 2.3 | 38.3-282.2 | 118.8 | 1.6-20.8 | 7.6 |
| New | 23.7-213.6 | 80.4 | 0.1-5.5 | 1.7 | 38.3-263.9 | 110.8 | 1.6-14.6 | 6.8 |
| Retrofit | 29.4-157.4 | 79.7 | 0.5-13.0 | 4.5 | 60.4-282.2 | 139.3 | 4.3-20.8 | 9.7 |
| Salable | 132.8-185.0 | 153.1 | 13.0-13.0 | 13.0 | 254.6-282.2 | 271.6 | 16.7-20.8 | 18.1 |
| Throwaway | 23.7-313.6 | 75.8 | 0.1-11.3 | 2.1 | 38.3-263.9 | 110.9 | 1.6-17.6 | 7.0 |

TABLE 9. ADJUSTED CAPITAL AND ANNUAL COSTS FOR OPERATIONAL FGD SYSTEMS BY PROCESS TYPE

| | Reported | | | | Adjusted | | | |
|---|---|---|---|---|---|---|---|---|
| | Capital | | Annual | | Capital | | Annual | |
| | Range, $/kW | Average, $/kW | Range, mills/kWh | Average, mills/kWh | Range, $/kW | Average, $/kW | Range, mills/kWh | Average, mills/kWh |
| Limestone | 2.37-170.4 | 67.9 | 0.1-7.8 | 1.6 | 38.3-194.3 | 98.9 | 1.6-14.6 | 6.1 |
| Lime | 29.4-213.6 | 81.8 | 0.3-11.3 | 3.2 | 60.4-210.0 | 116.5 | 4.0-17.6 | 8.1 |
| Dual alkali | 47.2-174.8 | 97.8 | 1.3-1.3 | 1.3 | 87.8-263.9 | 146.7 | 5.0-13.9 | 8.7 |
| Lime/alkaline fly ash | 43.4-173.8 | 93.9 | 0.4-5.4 | 2.1 | 52.5-184.4 | 122.8 | 3.0-14.1 | 7.2 |
| Sodium carbonate | 42.9-100.8 | 69.2 | 0.2-0.5 | 0.4 | 87.1-150.9 | 110.9 | 5.8-7.4 | 6.4 |
| Wellman Lord | 132.8-185.0 | 153.1 | 13.0-13.0 | 13.0 | 254.6-282.2 | 271.6 | 16.7-20.8 | 18.1 |
| Limestone/alkaline fly ash | 49.3-49.3 | 49.3 | 0.8-0.8 | 0.8 | 102.6-102.6 | 102.6 | 5.4-5.4 | 5.4 |

TABLE 10. REPORTED AND ADJUSTED CAPITAL AND ANNUAL COSTS FOR OPERATIONAL FGD SYSTEMS (CON'T)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| South Mississippi Electric Power | | | | | | | | |
| R. D. Morrow, Sr. 1 | 10,896,000 | 53.7 | NA | NA | 24,047,200 | 118.5 | 7,115,990 | 6.94 |
| R. D. Morrow, Sr. 2 | 10,896,000 | 53.7 | NA | NA | 24,047,200 | 118.5 | 7,115,990 | 6.94 |
| Southern Illinois Power | | | | | | | | |
| Marion 4 | 15,200,930 | 87.9 | 859,453 | 0.98 | 20,906,447 | 120.8 | 7,107,823 | 7.75 |
| Southern Indiana Gas & Electric | | | | | | | | |
| A. B. Brown 1 | 12,496,000 | 47.2 | 1,850,565 | 1.30 | 23,414,388 | 88.4 | 7,094,130 | 4.98 |
| Springfield City Utilities | | | | | | | | |
| Southwest 1 | 16,744,500 | 86.3 | 778,749 | 1.20 | 27,822,607 | 143.4 | 8,092,238 | 8.21 |
| Springfield Water, Light & Power | | | | | | | | |
| Dallman 3 | 34,923,800 | 170.4 | 4,381,500 | 4.68 | 39,829,200 | 194.3 | 15,913,700 | 14.56 |
| Tennessee Valley Authority | | | | | | | | |
| Widows Creek 8 | 47,900,000 | 87.1 | 14,576,400 | 7.76 | 86,968,828 | 158.1 | 21,379,073 | 7.28 |
| Utah Power & Light | | | | | | | | |
| Hunter 1 | 24,400,000 | 56.7 | NA | NA | 32,294,620 | 75.1 | 10,614,532 | 4.66 |
| Hunter 2 | 25,880,000 | 60.2 | 1,072,600 | 0.32 | 31,225,000 | 72.6 | 10,355,700 | 4.55 |
| Huntington 1 | 2,709,000 | 63.0 | 2,946,400 | 1.27 | 38,698,607 | 90.0 | 13,411,652 | 5.89 |

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7. Flue Gas Desulfurization Information System (FGDIS). Computerized data base. U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, NC. Access to FGDIS can be obtained through Walter Finch, NTIS, 5285 Port Royal Road, Springfield, VA 22161.

# TABLE 10. REPORTED AND ADJUSTED CAPITAL AND ANNUAL COSTS FOR OPERATIONAL FGD SYSTEMS

| | Reported | | | | Adjusted | | | |
|---|---|---|---|---|---|---|---|---|
| | Capital | $/kW | Annual | mills/kWh | Capital | $/kW | Annual | mills/kWh |
| Alabama Electric | | | | | | | | |
| Tombigbee 2 | 6,921,100 | 27.4 | 434,929 | 0.33 | 9,756,200 | 38.3 | 4,249,650 | 3.18 |
| Tombigbee 3 | 6,992,100 | 27.4 | 434,929 | 0.33 | 9,756,200 | 38.3 | 4,249,650 | 3.18 |
| Arizona Electric Power | | | | | | | | |
| Apache 2 | 8,148,069 | 41.8 | 51,784 | 0.10 | 13,171,700 | 67.5 | 3,739,900 | 3.75 |
| Apache 3 | 7,214,052 | 37.0 | 51,784 | 0.10 | 11,661,900 | 59.8 | 3,739,900 | 3.75 |
| Arizona Public Service | | | | | | | | |
| Cholla 1 | 6,550,000 | 52.0 | NA | NA | 10,245,100 | 81.3 | 4,608,800 | 4.79 |
| Cholla 2 | 44,352,000 | 168.0 | 1,003,568 | 0.75 | 42,787,600 | 162.1 | 10,998,300 | 8.22 |
| Central Illinois Light | | | | | | | | |
| Duck Creek 1 | 31,125,000 | 74.8 | 10,851,000 | 5.04 | 55,001,000 | 132.2 | 12,433,100 | 5.78 |
| Central Illinois Public Service | | | | | | | | |
| Newton 1 | 107,831,000 | 174.8 | NA | NA | 162,847,600 | 263.9 | 45,624,900 | 13.94 |
| Colorado Ute Electric | | | | | | | | |
| Craig 1 | 38,613,500 | 86.5 | 462,600 | 0.53 | 48,179,000 | 105.9 | 12,148,300 | 5.33 |
| Craig 2 | 32,810,500 | 73.5 | 1,128,400 | 0.46 | 41,070,100 | 90.3 | 10,382,700 | 4.56 |
| Columbus & Southern Ohio Electric | | | | | | | | |
| Conesville 5 | 20,663,500 | 50.3 | 8,670,530 | 5.52 | 40,857,200 | 99.4 | 14,475,100 | 6.78 |
| Conesville 6 | 20,663,500 | 50.3 | 8,670,530 | 5.52 | 40,857,200 | 99.4 | 14,475,100 | 6.78 |
| Cooperative Power Association | | | | | | | | |
| Coal Creek 1 | 23,650,000 | 43.4 | 1,166,200 | 0.41 | 28,633,100 | 52.5 | 8,414,350 | 2.99 |
| Coal Creek 2 | 23,650,000 | 43.4 | 1,166,200 | 0.41 | 28,633,100 | 52.5 | 8,414,350 | 2.99 |
| Duquesne Light | | | | | | | | |
| Elrama 1-4 | 61,320,000 | 120.2 | 21,027,451 | 7.18 | 95,755,400 | 187.8 | 35,731,700 | 12.89 |
| Phillips 1-6 | 52,055,000 | 127.0 | 18,301,000 | 11.00 | 86,097,500 | 210.0 | 35,731,700 | 17.65 |
| Indianapolis Power & Light | | | | | | | | |
| Petersburg 3 | 55,820,000 | 104.9 | NA | NA | 86,227,500 | 162.1 | 28,565,000 | 9.74 |
| Kansas City Power & Light | | | | | | | | |
| Hawthorn 3 | 3,220,000 | 29.4 | 346,441 | 1.15 | 6,909,850 | 62.8 | 2,912,100 | 5.25 |
| Hawthorn 4 | 3,220,000 | 29.4 | 346,441 | 1.15 | 6,909,850 | 62.8 | 2,912,100 | 5.25 |
| LaCygne 1 | 46,900,000 | 53.7 | 8,060,047 | 5.38 | 87,498,400 | 100.1 | 52,735,300 | 11.29 |
| Kansas Power & Light | | | | | | | | |
| Jeffrey 1 | 27,306,900 | 37.9 | 321,000 | 0.11 | 39,710,500 | 55.9 | 9,353,200 | 2.42 |
| Jeffrey 2 | 26,458,800 | 37.8 | 949,900 | 0.29 | 28,840,100 | 41.2 | 6,396,400 | 1.65 |
| Kentucky Utilities | | | | | | | | |
| Green River 1-3 | 3,966,155 | 62.0 | 364,005 | 5.20 | 7,510,600 | 117.8 | 3,754,800 | 10.99 |
| Louisville Gas & Electric | | | | | | | | |
| Cane Run 4 | 12,647,000 | 66.6 | 960,301 | 1.29 | 21,882,500 | 115.2 | 6,422,400 | 6.20 |
| Cane Run 5 | 13,759,000 | 68.8 | 763,443 | 0.92 | 20,476,600 | 102.4 | 5,784,300 | 5.30 |
| Cane Run 6 | 20,596,900 | 71.5 | NA | NA | 25,290,600 | 87.8 | 11,073,000 | 7.23 |
| Mill Creek 1 | 17,661,500 | 55.0 | NA | NA | 21,627,800 | 60.4 | 8,107,100 | 4.26 |
| Mill Creek 3 | 18,846,880 | 42.6 | 321,463 | 1.25 | 29,163,000 | 66.0 | 9,636,200 | 4.03 |
| Paddy's Run 6 | 4,320,000 | 61.7 | NA | NA | 9,307,300 | 133.0 | 4,430,300 | 12.25 |
| Minnesota Power & Light | | | | | | | | |
| Clay Boswell 4 | 86,900,000 | 173.8 | 18,844,512 | 5.38 | 102,165,300 | 184.4 | 40,437,300 | 14.09 |
| Minnkota Power | | | | | | | | |
| Milton R. Young 2 | 44,119,600 | 100.3 | 754,445 | 0.53 | 68,487,500 | 155.7 | 14,966,000 | 5.44 |
| Monongahela Power | | | | | | | | |
| Pleasants 1 | 81,452,400 | 119.1 | 5,532,800 | 1.46 | 104,562,000 | 152.9 | 27,951,300 | 7.94 |
| Pleasants 2 | 81,452,400 | 119.1 | 5,532,800 | 1.46 | 104,562,000 | 152.9 | 27,951,300 | 7.94 |
| Montana Power | | | | | | | | |
| Colstrip 1 | 36,500,000 | 101.4 | 6,128,000 | 2.97 | 52,519,850 | 145.9 | 15,642,050 | 8.27 |
| Colstrip 2 | 36,500,000 | 101.4 | 6,128,000 | 2.97 | 52,519,850 | 145.9 | 15,642,050 | 8.27 |
| Nevada Power | | | | | | | | |
| Reid Gardner 1 | 5,363,375 | 42.9 | 251,514 | 0.46 | 10,891,350 | 87.1 | 3,617,450 | 5.78 |
| Reid Gardner 2 | 5,363,375 | 42.9 | 251,514 | 0.46 | 10,891,350 | 87.1 | 3,617,450 | 5.78 |
| Reid Gardner 3 | 12,599,160 | 100.8 | 131,824 | 0.23 | 18,866,173 | 150.9 | 4,637,163 | 7.40 |
| Northern Indiana Public Service | | | | | | | | |
| Dean H. Mitchell 11 | 18,192,040 | 157.4 | 2,414,589 | 13.02 | 29,431,808 | 254.6 | 11,129,239 | 20.79 |
| Northern States Power | | | | | | | | |
| Sherburne 1 | 34,892,020 | 49.3 | 2,716,759 | 0.75 | 73,854,486 | 102.6 | 21,018,195 | 5.43 |
| Sherburne 2 | 34,982,020 | 49.3 | 2,716,659 | 0.75 | 73,854,486 | 102.6 | 21,018,195 | 5.43 |
| Pacific Power & Light | | | | | | | | |
| Jim Bridger 4 | 49,643,000 | 90.3 | NA | NA | 65,113,736 | 118.4 | 19,681,160 | 6.81 |
| Pennsylvania Power | | | | | | | | |
| Bruce Mansfield 1 | 110,639,000 | 120.7 | 9,979,900 | 3.28 | 132,234,039 | 144.2 | 53,122,918 | 11.31 |
| Bruce Mansfield 2 | 110,639,000 | 120.6 | 9,979,900 | 3.28 | 132,234,039 | 144.2 | 53,122,918 | 11.31 |
| Bruce Mansfield 3 | 195,857,200 | 213.6 | 11,575,300 | 3.11 | 166,043,400 | 181.1 | 48,255,200 | 10.27 |
| Public Service of New Mexico | | | | | | | | |
| San Juan 1 | 47,944,400 | 132.8 | NA | NA | 100,333,473 | 277.9 | 29,836,802 | 16.69 |
| San Juan 2 | 47,985,000 | 137.1 | NA | NA | 98,777,569 | 282.2 | 29,423,764 | 16.89 |
| Salt River Project | | | | | | | | |
| Coronado 1 | 32,624,500 | 79.4 | 1,788,000 | 0.85 | 35,560,700 | 86.5 | 15,339,100 | 7.70 |
| Coronado 2 | 32,624,500 | 79.4 | 1,788,000 | 0.85 | 35,560,700 | 86.5 | 15,339,100 | 7.70 |
| South Carolina Public Service | | | | | | | | |
| Winyah 2 | 6,646,098 | 23.7 | 527,000 | 0.29 | 13,148,872 | 47.0 | 2,697,896 | 1.84 |
| Winyah 3 | 10,742,500 | 38.4 | NA | NA | 18,846,700 | 66.6 | 6,926,700 | 4.83 |

## SESSION 2: ECONOMICS

Chairman: Thomas M. Morasky
Reliability and Nonrecovery Systems
Electric Power Research Institute
Palo Alto, CA

# COMPUTER ECONOMICS OF PHYSICAL COAL CLEANING AND FLUE GAS DESULFURIZATION

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## ABSTRACT

A computer model that simulates the performance and calculates the economics of a coal-cleaning process, a flue gas desulfurization (FGD) process, and a combination of the two processes for electric utility boilers has been developed by the Tennessee Valley Authority (TVA) under sponsorship of the U.S. Environmental Protection Agency (EPA). The model also determines other economic benefits and penalties to overall power plant operations that are associated with the use of cleaned coal. The model is described and its use is illustrated for selected design and economic premises. The present status of the model is assessed and possible future studies are discussed. The illustrative examples show that in some instances a combination of coal cleaning and FGD for $SO_2$ emission control can be more economical than FGD alone.

For the cases studied, it was found that the use of coal cleaning in combination with FGD can have a varied effect on the levelized annual cost of power production. This effect, which is dependent on the coal and the specific operating conditions, ranges from a 0.5 percent increase to a 22.6 percent decrease in those costs.

The methods used to determine many of the other economic benefits and penalties of coal cleaning are necessarily general in nature because detailed data relating specific coal properties to boiler performance and operating costs are scarce. Thus, development and incorporation of more detailed and quantitative data in the model would greatly increase the usefulness of the model in assessing overall economic effects of coal cleaning.

## INTRODUCTION

In recent years, coal cleaning has come to be regarded as a practical alternative in many cases for the control of $SO_2$ emissions from coal-fired power plants. TVA recently completed an economic evaluation for EPA that demonstrated the potential of coal cleaning in $SO_2$ emission control (1). As a continuation of this program, a computer model was developed to simulate the performance and economics of full-scale coal cleaning alone and in combination with limestone and lime FGD (2,3). The model determines the process design and economics for a coal-cleaning process, an FGD process, or a coal-cleaning process combined with FGD. It also determines other economic benefits and penalties attributable to the use of cleaned coal.

The model should be useful in comparisons of the design and costs of various combinations of coal-cleaning and lime or limestone FGD processes. This should be particularly useful when evaluating processes for specific applications because the model will illustrate the effect of changes in process variables on the design and cost of the component processes or the entire system as a whole.

## MODEL DESCRIPTION

The coal-cleaning/FGD computer model consists of four separate computer programs, which are linked by common input and output data. The first program determines the design and economics of the coal-cleaning process; the second and third programs determine the FGD process design and economics. The fourth program quantifies selected economic benefits and penalties of using cleaned coal. Unlike the first three programs, which are modified versions of previously developed programs, the fourth program has been developed specifically for this project. The model is written in FORTRAN IV and was run on an IBM model 3083 computer.

The cost elements that the model calculates include the capital investment, first-year annual revenue requirements, and levelized annual revenue requirements; each element can be generated for a coal-cleaning process, an FGD process, or a combined coal-cleaning/FGD process. In the case of the combined coal-cleaning/FGD process, an incremental cost is also calculated which is the difference between the cost for the coal-cleaning process and any net benefit realized from the use of cleaned coal (including any reduction in the FGD costs).

## COAL-CLEANING PROGRAM

The coal-cleaning program is the primary control program (see Figure 1). It was adapted from a program developed by the University of Pittsburgh and the Bureau of Mines, and modified by Battelle Columbus Laboratories. The Battelle version, known as the Coal Preparation Simulation Model Version 4 (CPSM4) (4), was obtained from Versar, Inc., who also provided valuable assistance in its adaptation to the TVA computer system. The program required many modifications to conform to the TVA process design criteria and to form the combined coal-cleaning/FGD model. Although many of these changes were relatively minor and did not alter the program processing sequence, some areas required major revisions, necessitating the addition of five new subroutines and the associated rearrangement of the program.

This program is capable of simulating many coal-cleaning processes provided that equipment performance, process design, and economic data are available. The process design used in the illustrative runs for this paper is felt to be a typical application. A flow diagram for this process design is shown in Figure 2. The process, as illustrated, separates the raw coal into three size fractions, each of which is processed in a different type of separation equipment. The coarse coal is cleaned in a dense-medium vessel, the intermediate coal in a dense-medium cyclone, and the fine coal in froth flotation cells.

## FGD MODEL

The FGD model is the Shawnee lime/limestone computer model developed by Bechtel National, Inc., and TVA using data obtained from the test facility at the TVA Shawnee Steam Plant near Paducah, Kentucky (5). This model consists of two programs that produce full-scale design and economic data for a variety of limestone or lime FGD systems.

The current model includes options for limestone or lime scrubbing: a mobile-bed absorber (TCA), a spray tower, or a venturi/spray tower absorber, and various waste disposal methods. The FGD process design used to illustrate the capabilities of the combined model is illustrated in Figure 3. The process employs limestone slurry scrubbing in a spray tower absorber, and the untreated waste is disposed of in a pond.

## ECONOMIC BENEFITS AND PENALTIES PROGRAM

There are many differences between cleaned coal and raw coal that result in economic benefits and penalties for a power plant that uses cleaned coal. This program utilizes appropriate equations to approximate many of the benefits and penalties that accrue because of such differences as the lower ash content, the higher moisture content, and the generally higher heating value of the cleaned coal. Each of the benefits and penalties calculated by this program is discussed below.

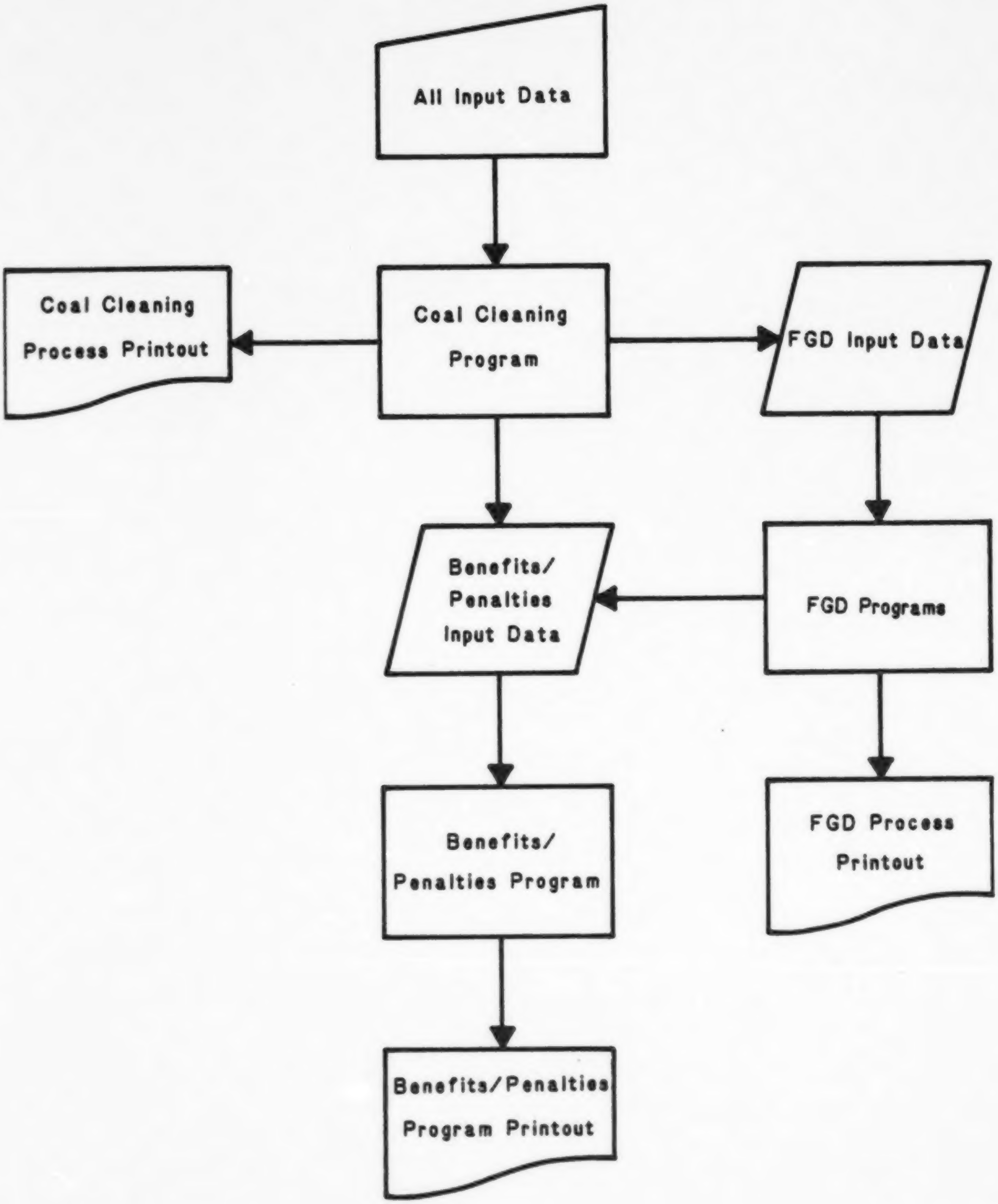
All Input Data
Coal Cleaning Process Printout
Coal Cleaning Program
FGD Input Data
Benefits/ Penalties Input Data
FGD Programs
Benefits/ Penalties Program
FGD Process Printout
Benefits/Penalties Program Printout

Figure 1. Flow of data through the combined model.

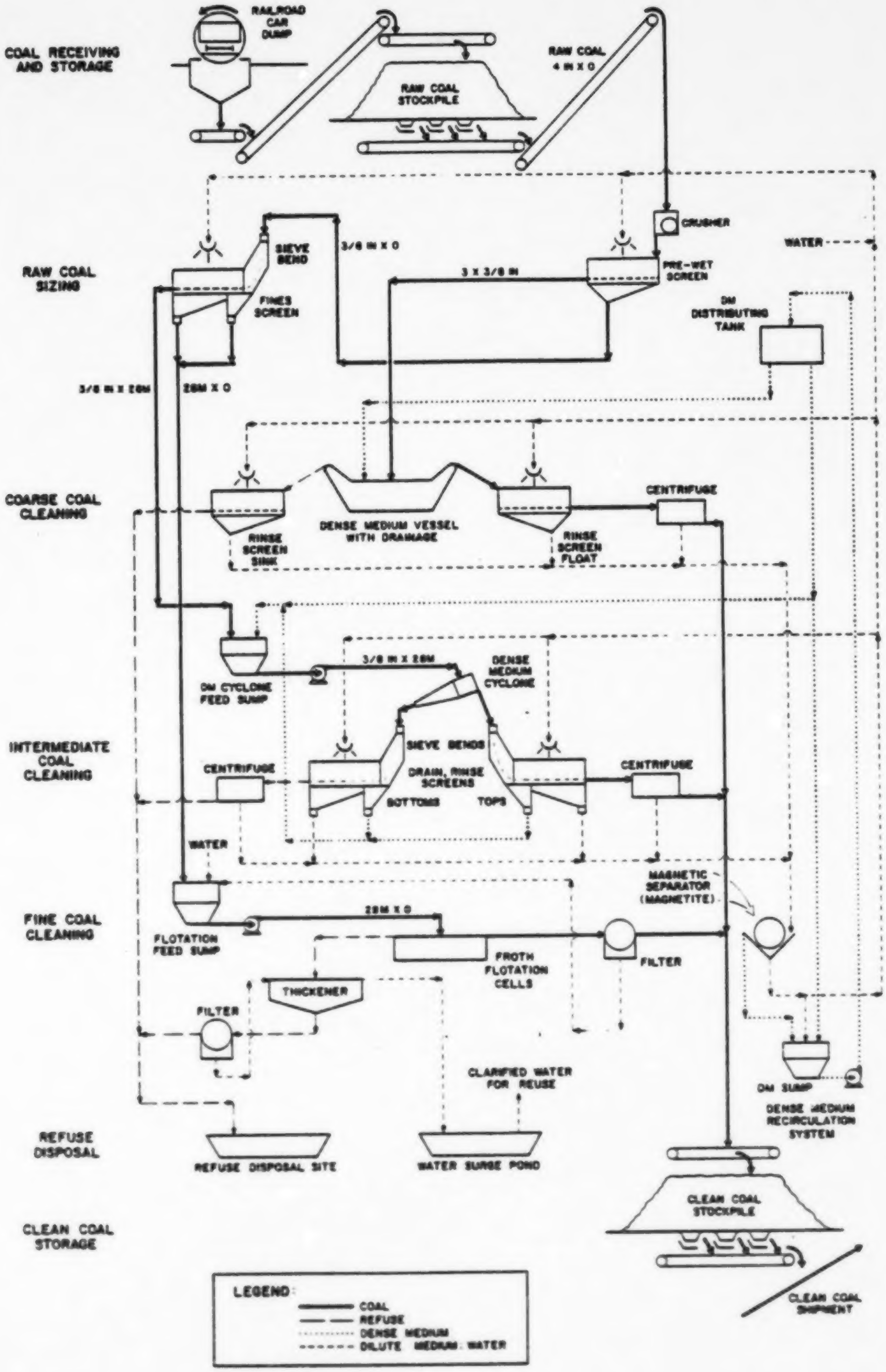

Figure 2. Flow diagram for the coal-cleaning process.

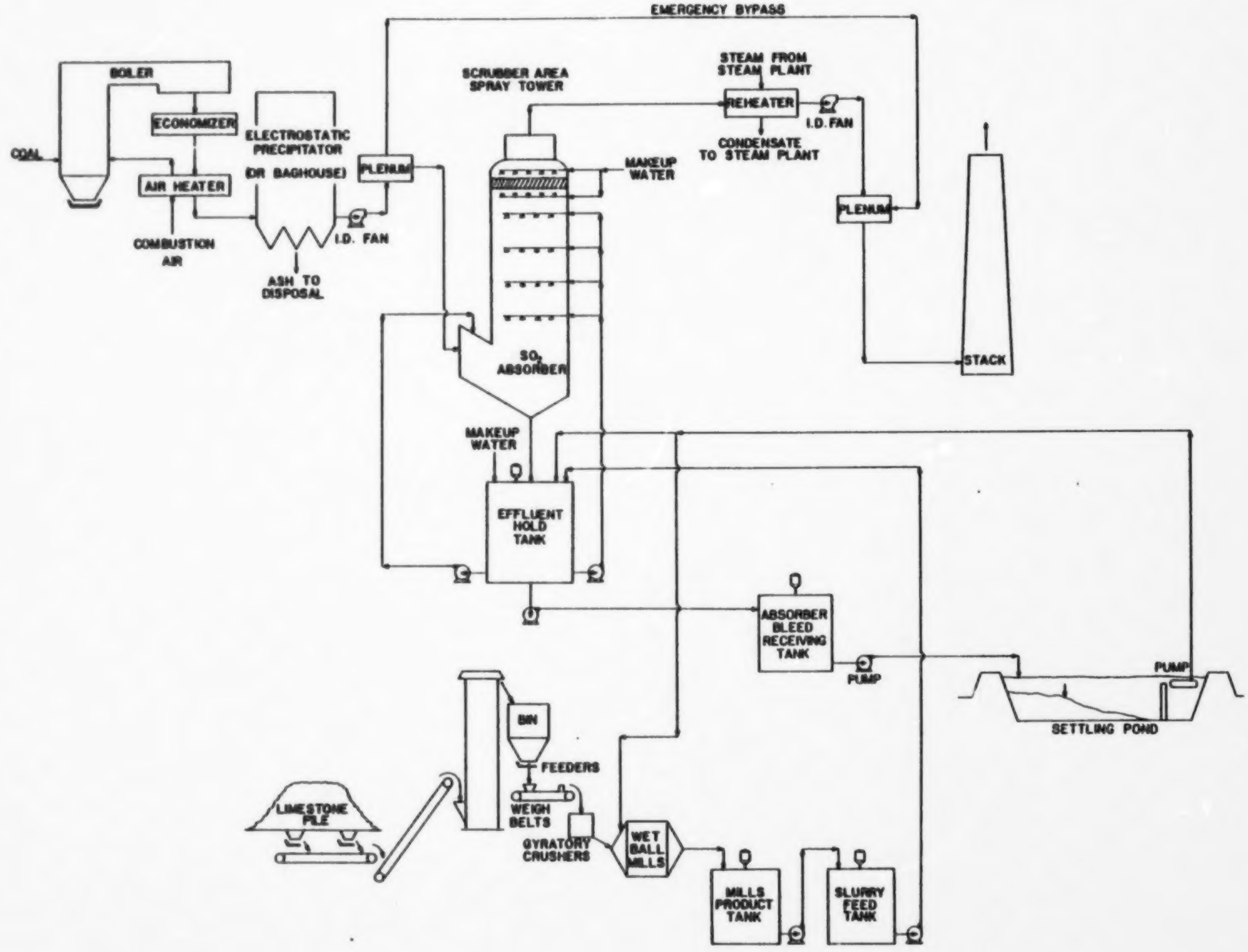

Figure 3. Flow diagram for the limestone-scrubbing FGD process.

### FGD Costs

The most important effect of coal cleaning on power plant costs is in the area of FGD costs. In some cases coal cleaning or coal cleaning with FGD can be more economical than FGD alone in controlling $SO_2$ emissions. The lower sulfur content and increased heating value of cleaned coal reduce the quantity of $SO_2$ produced in the combustion process, thus reducing the $SO_2$ removal requirement of the FGD process. There are some cases where the use of cleaned coal can even eliminate the need for FGD. FGD cost benefits which accrue from coal cleaning are determined by comparing costs required when FGD is used to control $SO_2$ emissions from raw versus clean coal.

### Raw Coal Loss

No presently available coal-cleaning process is capable of achieving 100 percent separation of pure coal from its impurities. There is some coal lost in the cleaning plant refuse and some impurities remain in the cleaned coal. The coal that is lost is an economic liability for the coal-cleaning plant. This liability or penalty can be estimated by the fraction or percentage of the feed coal heat content that is recovered in the product coal (Btu recovery).

### Transportation Costs

Coal cleaning results in a product that has a higher heating value than the raw coal, thereby reducing the weight of coal necessary to satisfy the heat requirements of a specific power plant. A transporation cost reduction or benefit occurs when coal cleaning is performed at the mine.

### United Mine Workers' (UMW) Pension Fund Benefits

The provisions of the 1978 UMW contract require mine operators to pay $1.385 to the Pensions and Benefit Trust Fund for every ton of coal shipped to a consumer (6). Since coal cleaning generally reduces the quantity of coal required by a power plant, the contribution to the trust fund is also reduced, thereby resulting in a cost benefit for the utility.

### State Taxes

State-imposed coal taxes, often called severance taxes, are presently levied by the legislatures of 13 states (7). Depending upon the method of taxation, coal cleaning can reduce or increase these taxes, thus creating a cost benefit or penalty. There are currently four different methods which are based upon (1) the tons of coal shipped, (2) the value of coal shipped, (3) the tons of coal mined, and (4) the value of coal mined. The model is capable of simulating any of the four; however, taxation based on the tonnage of coal shipped is the most common and is used in the example runs for this paper. This method will generally provide an economic benefit because cleaned coal as compared with ROM coal will result in a reduction in the tonnage of coal shipped.

### Size Reduction

In general, at least two and sometimes three size reduction operations are performed on coal as it moves from the coal seam to the power plant boiler. For the development of this program, it was assumed that the power plant was equipped with pulverized coal boilers in which case three separate size reduction operations are necessary. The first operation is performed at the mine where the run-of-mine (ROM) coal is crushed to an appropriate topsize. The next two operations are performed at the power plant where the coal is crushed before being fed to the pulverizers and finely ground. When coal cleaning is used, an additional size reduction operation is usually included at the cleaning plant, resulting in a cost benefit to the utility because the size reduction requirements at the power plant are reduced. Coal cleaning can also produce a benefit in the size reduction operations at the power plant by reducing the coal mineral matter, making the coal easier to grind. A third consideration is the increased heating value of cleaned coal, which decreases the amount to be ground. One effect of coal cleaning, the increase in surface moisture, can increase pulverizer plugging, but it is not considered in the program because of lack of data on the effects of moisture on pulverizer operation.

### Maintenance Costs

The quality and quantity of the coal used in a power plant have long been recognized as having a direct effect on the maintenance costs of the plant equipment. Some of the equipment areas have been mentioned in the preceding paragraphs, but other areas which must be considered include the boilers and accessories, coal conveying and storage equipment, and the air heaters. Coal cleaning yields an economic benefit in maintenance costs for these and other areas of power plant operation by raising the quality of coal burned in the plant through the reduction of the ash and sulfur content. To quantify this benefit the program uses a relationship based on the ash and sulfur in the coal, which is derived from actual power plant maintenance data (8).

### Power Plant Availability

The availability of a power plant for the production of electricity is another area that is affected by the use of cleaned coal. Many of the factors relating to availability, such as tube corrosion, soot blower failure, slagging, and fouling, are influenced by the mineral content of the coal burned; therefore, they are also influenced by the use of cleaned coal. It is difficult to quantify the effects of coal cleaning on availability because factors unrelated to fuel quality tend to mask them. In the program, these effects (which are benefits in all cases) are quantified through the use of a logarithmic relationship based on the ash and sulfur in the coal (9).

### Boiler Efficiency

The efficiency of a power plant boiler is often expressed in terms of the amount of heat required to generate 1 kWh of power. This characteristic of the power plant is affected by coal cleaning in much the same manner as availability, with one notable exception: the increased surface moisture, inherent in cleaned coal, reduces boiler efficiency. Conversely, for a given coal the boiler efficiency generally increases as the amount of ash in the coal decreases. Less heat is lost to the boiler ash and the fouling and slagging of boiler heat transfer surfaces generally decrease. One additional factor affecting efficiency, but not related to coal cleaning, is the age of the boiler. Factors included in the equation used to quantify the effect of coal cleaning include coal moisture content, coal ash content, and boiler age (9). The ash content term accounts only for boiler ash heat loss.

### Electrostatic Precipitation

The major factor controlling the size and cost of an electrostatic precipitator (ESP) is the specific collection area, which is determined primarily by the dust loading and fly ash resistivity. Fly ash resistivity is related to such factors as ash composition and sulfur content in the coal. Dust loading is affected by coal ash content and boiler type. Coal cleaning, by altering these coal properties, also affects the ESP cost. In some cases, the reduction in dust loading associated with lower ash content does not compensate for the increase in resistivity associated with reduced sulfur content.

### Ash Disposal

The costs of transporting and disposing of ash produced by coal combustion are decreased because coal cleaning reduces the ash content and increases the heating value of the coal. Both of these factors decrease the quantity of ash to be disposed of at the power plant.

## DESIGN AND ECONOMIC PREMISES

The base case used in illustrating this model assumes a new, midwestern, 1,000-MW, pulverized-coal-fired power plant supplied by a coal-cleaning plant at a mine 500 miles away, with transportation by unit train. The raw coal design heat rate of the boiler is 9,200 Btu/kWh and it operates at full load for 5,500 hours a year over a 30-year life.* The coal-cleaning process incorporates three cleaning streams: dense-medium vessels for coarse coal (3 in. x 3/8 in.), dense-medium cyclones for medium-sized coal (3/8 in. x 28 mesh), and froth flotation for fine coal (less than 28 mesh).

The economic premises are based on regulated utility operations. Capital investments, first-year annual revenue requirements, and levelized annual revenue requirements are determined. The costs are based on 1982 for capital investment and 1984 for annual revenue requirements.

## ILLUSTRATIVE EXAMPLES OF MODEL USE

The results obtained from this model can be used in many different ways, some of which are listed on the following page:

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*English to metric conversion factors are given at the end of this text.

- To illustrate the effects of changes in process conditions on the performance and economics of a coal-cleaning, an FGD, or a combined coal-cleaning/FGD process.

- To determine the most economical method of $SO_2$ control using coal cleaning, FGD, or a combination of both.

- To analyze the probable effects of coal cleaning on power plant operations and economics by considering various benefits and penalties attributable to coal cleaning.

- To compare the performance and economics for different coals, coal-cleaning process variables, and FGD process variables.

The main objectives of the report, from which this paper is derived, are to make potential users of this model aware of its availability and to illustrate some possible uses. To accomplish the latter, the model was used to simulate a range of coal properties, cleaning conditions, power plant variables, and emission requirements. Eighty runs were made using four coals, each cleaned at four specific gravities of separation, with the flue gas restricted to five $SO_2$ emission limits. Other cases were run by varying conditions such as cleaned coal topsize, power plant megawatt rating, and distance from the cleaning plant to the power plant.

## COALS AND EMISSION LIMITS

The illustrative cases are based on four coals, selected characteristics of which are presented in Table 1. Each of these coals was cleaned by controlling the specific gravity of the separating media at 1.40, 1.50, 1.60, and 1.80. The emission standards evaluated consist of 0.6, 1.2, 2.0, and 4.0 lb $SO_2$/MBtu emission limits and the 1979 New Source Performance Standards (NSPS).

## COAL-CLEANING OPERATING PERFORMANCE

In a coal-cleaning plant the specific gravity of separation is the operating condition usually controlled to regulate the properties of the cleaned coal. It affects the Btu recovery of the plant and the reduction in potential $SO_2$ emissions.

The Btu recovery is a useful parameter for describing the effects of specific gravity of separation on coal cleaning costs. It is a measure of the raw and clean coal properties which incorporate the dual effects of yield and Btu enhancement. For a given plant design and plant capacity the two variables which most strongly influence the cost of cleaned coal are the plant yield (weight recovery of clean coal from ROM coal) and the ash reduction or Btu enhancement of the product. The capital and operating expenses of the coal preparation plant are related to the amount of material which must be processed. The costs added to a ton of clean coal increase as the plant yield decreases; i.e., as more material must be mined, processed, and discarded as refuse. Although a decrease in the specific gravity of separation reduces the amount of material recovered, it increases the calorific value of the product.

TABLE 1. CHARACTERISTICS OF SELECTED COALS

| Coal characteristic | Illinois No. 6 coal | Pittsburgh coal | Upper Freeport coal | Cedar Grove coal |
|---|---|---|---|---|
| Sulfur, % | 4.34 | 3.67 | 2.32 | 0.85 |
| Ash, % | 29.39 | 13.81 | 16.80 | 16.04 |
| Moisture, % | 1.36 | 3.42 | 5.60 | 6.60 |
| Heat content, Btu/lb | 9,667 | 12,121 | 11,668 | 11,680 |
| Equivalent $SO_2$ content, lb $SO_2$/MBtu | 8.97 | 6.05 | 3.97 | 1.45 |

Basis: All values are for coal, as received
Source: Reference (10, 11).

With increased heating value, a customer needs to buy a smaller weight of coal to meet boiler heat requirements.

An important consideration for emission control applications is the reduction of potential $SO_2$ emission which can be achieved by coal cleaning. The emission reduction achievable by coal preparation depends on the raw coal properties (washability), degree of size reduction (crushing), the type of cleaning equipment, and the process conditions (specific gravity of separation). As the specific gravity of separation decreases, the amount of mineral contaminants (including pyritic sulfur) which is contained in the cleaned coal product decreases. This improved coal quality is, however, achieved at the expense of decreased Btu recovery.

The relationship between specific gravity of separation, the resulting Btu recovery, and reduction in potential $SO_2$ emission is shown in Table 2. Both the Btu recovery and the potential $SO_2$ emissions decrease as the specific gravity of separation is reduced. This is to be expected because the quantity of coal lost in the cleaning plant refuse increases as the specific gravity decreases. As the specific gravity of separation decreases, the sulfur reduction increases as a result of the increased pyritic sulfur removed. There is thus a tradeoff, illustrated in Figure 4, between high Btu recovery and high sulfur removal. Note that the raw and clean coal properties vary substantially from coal to coal. The clean coal properties are highly dependent on the coal washability (an inherent property) and the conditions of cleaning.

A further illustration of the effect of the operating specific gravity in the cleaning plant on the Btu recovery is provided in Figure 5. From this graph, one can see that the relationship between Btu recovery and operating specific gravity varies according to the type of coal being used. This variation can be more specifically attributed to the differences in washability of the coals. The values for coal washability are usually presented as tabulations of selected physical and chemical characteristics for a particular size fraction of the coal that sinks at one specific gravity and floats at a second higher specific gravity. These characteristics must include the weight fraction of the coal that floats at the particular specific gravity interval, expressed as a percentage of all the coal in the size fraction. Also required are the values for the percent ash, percent total sulfur, and the heating value of the floating coal. Percent pyritic sulfur is often included in the data, but it is not essential. A simplified version of the washability table for the Pittsburgh coal used in the illustrative runs is shown as an example in Table 3.

## FGD OPERATING PERFORMANCE

The FGD process design used to illustrate the model removes 90 percent of the $SO_2$ in the flue gas that is scrubbed. If the overall $SO_2$ removal requirement of the FGD system is less than 90 percent, a portion of the gas is bypassed to allow the scrubber to operate at the 90 percent removal level. The bypassed flue gas reduces the steam requirements for reheating because it is recombined with the scrubbed flue gas. For this reason, the amount of bypass is the most important FGD operating condition affecting the FGD design and cost. The portion of flue gas which can be bypassed is determined by the

TABLE 2. SULFUR REDUCTION AND BTU RECOVERY BY COAL CLEANING

| | Raw coal | Coal-cleaning operating, specific gravity | | | |
|---|---|---|---|---|---|
| | | 1.4 | 1.5 | 1.6 | 1.8 |
| Illinois No. 6 Coal | | | | | |
| lb $SO_2$/MBtu* | 8.97 | 3.86 | 4.18 | 4.38 | 5.08 |
| Sulfur reduction, % | - | 57 | 53 | 51 | 43 |
| Btu recovery, % | - | 78 | 88 | 92 | 96 |
| Pittsburgh Coal | | | | | |
| lb $SO_2$/MBtu | 6.05 | 3.79 | 4.18 | 4.37 | 4.68 |
| Sulfur reduction, % | - | 37 | 31 | 28 | 23 |
| Btu recovery, % | - | 82 | 92 | 95 | 97 |
| Upper Freeport Coal | | | | | |
| lb $SO_2$/MBtu | 3.97 | 1.76 | 1.93 | 2.03 | 2.35 |
| Sulfur reduction, % | - | 56 | 51 | 49 | 41 |
| Btu recovery, % | - | 78 | 89 | 93 | 97 |
| Cedar Grove Coal | | | | | |
| lb $SO_2$/MBtu | 1.45 | 1.17 | 1.20 | 1.23 | 1.25 |
| Sulfur reduction, % | - | 19 | 17 | 15 | 14 |
| Btu recovery, % | - | 91 | 93 | 95 | 96 |

*Assuming 100% conversion of sulfur to $SO_2$.

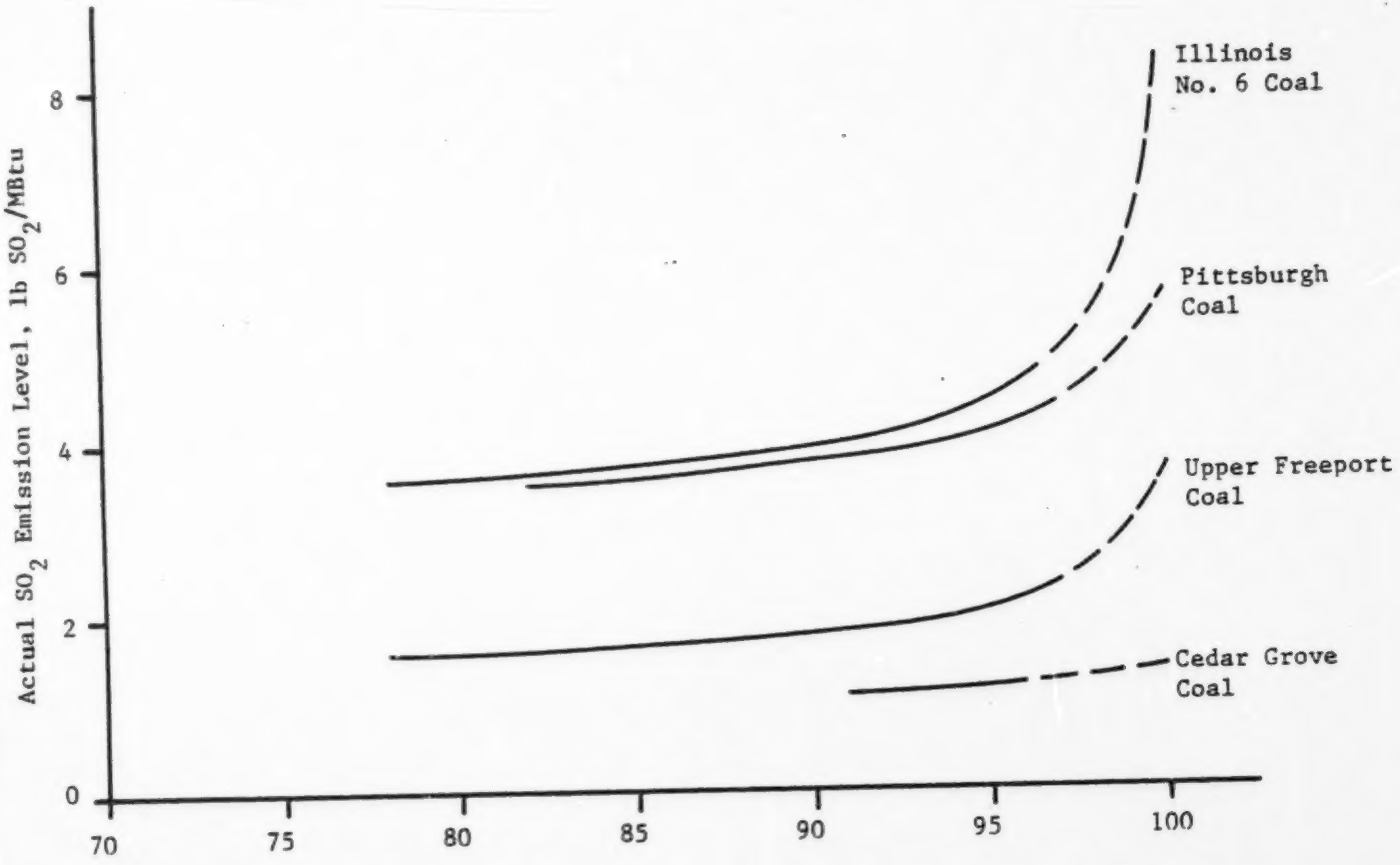


Figure 4. Effect of Btu recovery on the actual $SO_2$ emission levels.

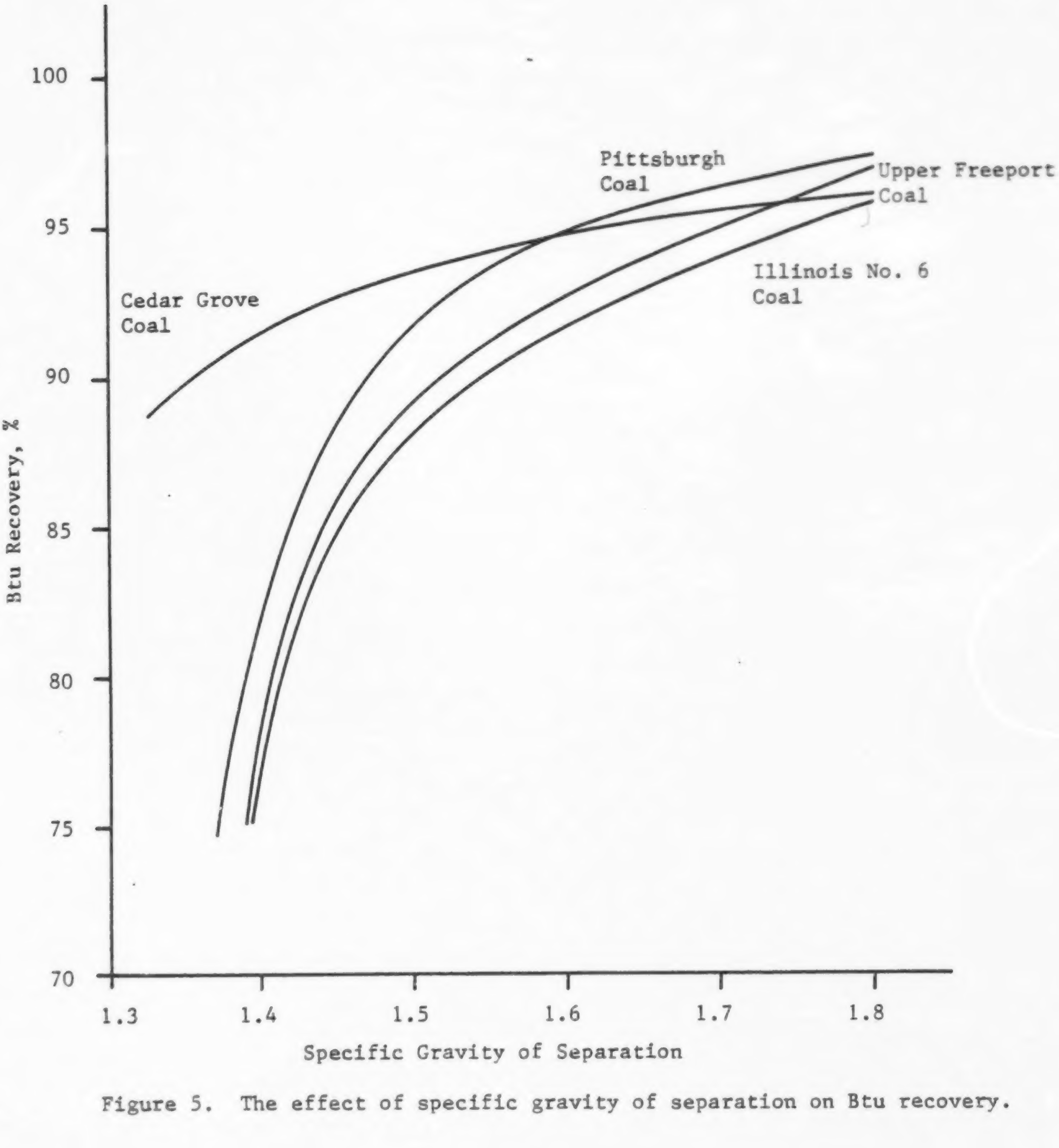


Figure 5. The effect of specific gravity of separation on Btu recovery.

TABLE 3. WASHABILITY DATA FOR THE PITTSBURGH COAL (4-INCH TOPSIZE)

| Specific gravity | Weight | Direct, percent<br>Ash | Direct, percent<br>Pyritic sulfur | Direct, percent<br>Total sulfur | Btu/lb | Cumulative, percent<br>Weight | Cumulative, percent<br>Ash | Cumulative, percent<br>Pyritic sulfur | Cumulative, percent<br>Total sulfur | Btu/lb |
|---|---|---|---|---|---|---|---|---|---|---|
| FLOAT-1.30 | 19.67 | 3.53 | 0.61 | 1.96 | 14,806 | 19.67 | 3.53 | 0.61 | 1.96 | 14,806 |
| 1.30-1.35 | 46.05 | 6.08 | 1.42 | 2.72 | 14,350 | 65.72 | 5.32 | 1.18 | 2.49 | 14,486 |
| 1.35-1.40 | 9.64 | 10.44 | 2.96 | 4.27 | 13,555 | 75.35 | 5.97 | 1.40 | 2.72 | 14,367 |
| 1.40-1.50 | 8.04 | 17.76 | 3.99 | 5.25 | 12,303 | 83.39 | 7.11 | 1.65 | 2.96 | 14,168 |
| 1.50-1.60 | 3.62 | 26.48 | 4.56 | 5.90 | 10,833 | 87.01 | 7.92 | 1.77 | 3.09 | 14,030 |
| 1.60-1.90 | 4.86 | 44.72 | 5.62 | 6.47 | 7,815 | 91.87 | 9.86 | 1.98 | 3.27 | 13,701 |
| 1.90-2.20 | 2.64 | 65.14 | 6.59 | 7.16 | 4,428 | 94.50 | 11.40 | 2.11 | 3.37 | 13,442 |
| 2.20-2.50 | 2.77 | 79.78 | 6.47 | 6.92 | 2,032 | 97.27 | 13.35 | 2.23 | 3.48 | 13,117 |
| 2.50-2.80 | 1.97 | 83.51 | 6.12 | 6.50 | 1,441 | 99.24 | 14.74 | 2.31 | 3.54 | 12,886 |
| 2.80-SINK | 0.76 | 63.58 | 32.81 | 34.59 | 3,195 | 100.00 | 15.11 | 2.54 | 3.77 | 12,812 |

Source: Reference (10)

emission limit, the heating value, the sulfur content of the fired coal, and the sulfur content of the ash. Figure 6 illustrates the effect that changes in operating specific gravity have on the amount of flue gas that can be bypassed. This set of curves (for the Pittsburgh coal) shows that the amount of flue gas bypassing the FGD scrubbers decreases as the operating specific gravity of the coal cleaning plant increases. This relationship is to be expected because of the comparatively higher sulfur content and lower heating value of coal cleaned at the higher specific gravities.

## ECONOMICS

The combined computer model is a useful aid in determining the combination of coal cleaning and FGD that will meet a specified emission limit at the minimum overall cost. The operating conditions for this minimum cost are not the same for every case because they can change with variations in different process characteristics (e.g., washing equipment efficiencies) and with the particular cost element chosen for the analysis.

### Capital Investment

The effects of changes in the degree of coal cleaning (in terms of Btu recovery) on (1) the capital investment required for the cleaning plant, (2) the change in FGD capital investment required, and (3) the capital investment benefits and penalties, are illustrated in Figure 7. The cases are for the Pittsburgh coal with a 1.20 lb $SO_2$/MBtu emission limit. In terms of change in capital investment, the degree of coal cleaning has a considerable effect on FGD capital investment and the net capital investment. Considering all three components, the capital investment is lower for the combined coal-cleaning/FGD process than for FGD alone over much of the range of Btu recoveries. This point is better understood if the net capital investment curve is considered to be the incremental capital investment required to implement a combined coal-cleaning/FGD process instead of using FGD alone. With this in mind the reader can consider any point on the net investment curve with a value less than zero to be a situation where combined coal-cleaning/FGD is less costly. The minimum in the net capital investment curve indicates the optimum level of coal cleaning with respect to capital investment. For the conditions used in Figure 7, this minimum occurs at a Btu recovery of about 75 percent. The specific gravity of separation equivalent to this recovery (approximately 1.37 from Figure 5) represents the conditions at which the system should be designed to minimize the capital investment.

### Annual Revenue Requirements

The relationships between the degree of coal cleaning and the various components of net levelized annual revenue requirements are presented in Figure 8 for the same cases that were used in Figure 7 for the total capital investment. A comparison of these figures shows that coal cleaning has the same general effect on FGD annual revenue requirements as it has on FGD capital investment, which is a continuing decline as the degree of coal cleaning increases (Btu recovery decreases). In the case of the other benefits and penalties, however, there is an initial decline as the degree of cleaning rises, followed by a rapid increase. This rise in costs can be

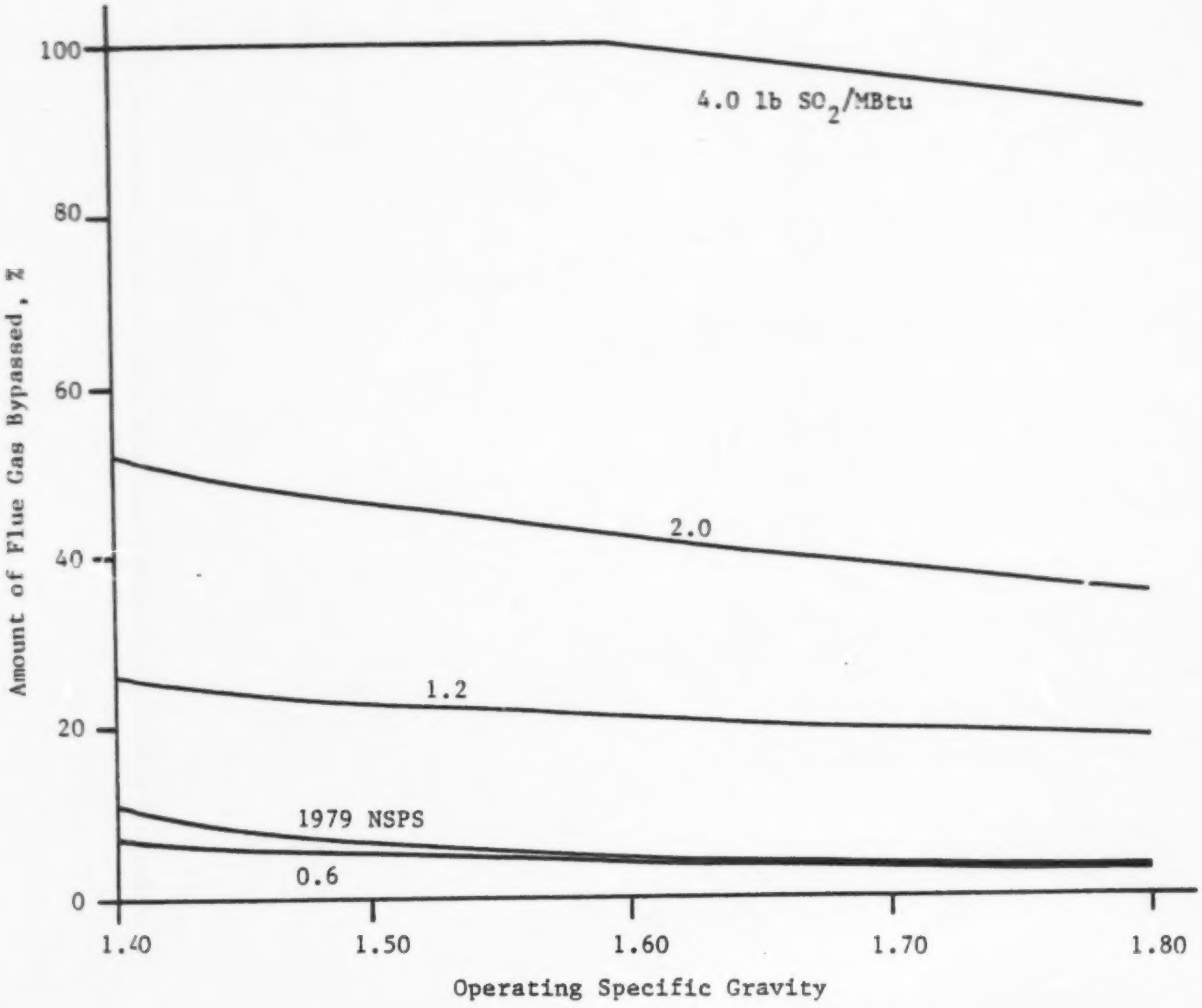


Figure 6. Effect of operating specific gravity at the cleaning plant on the flue gas bypassing the FGD process (Pittsburgh coal).

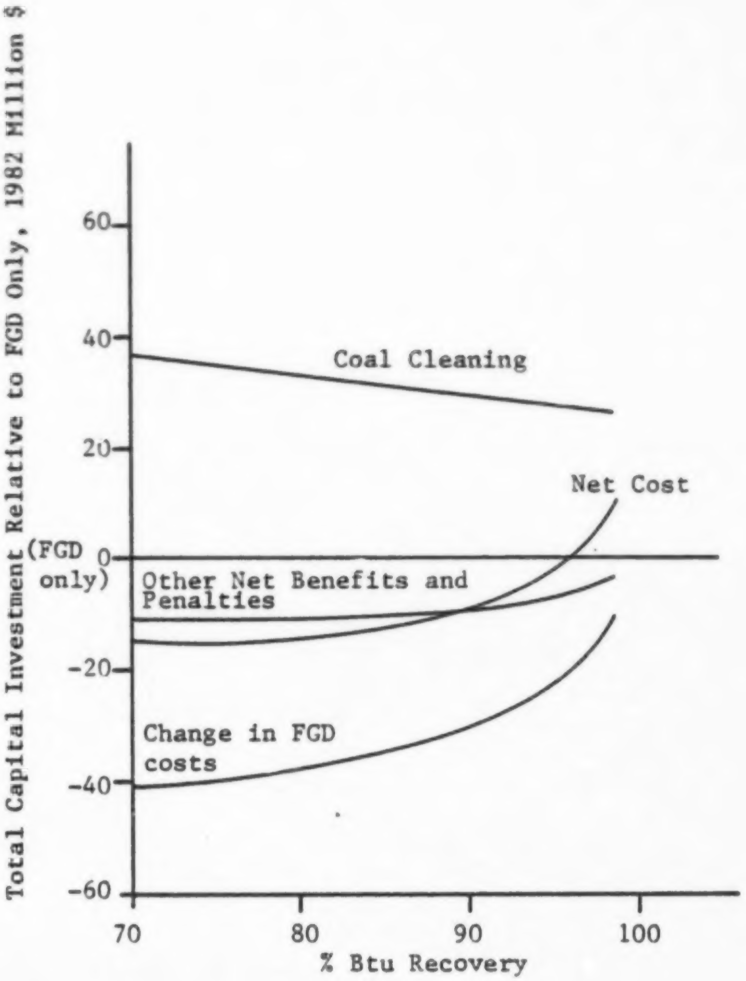


Figure 7. Effect of Btu recovery on the net total capital investment, Pittsburgh coal at 1.20 emission limit.

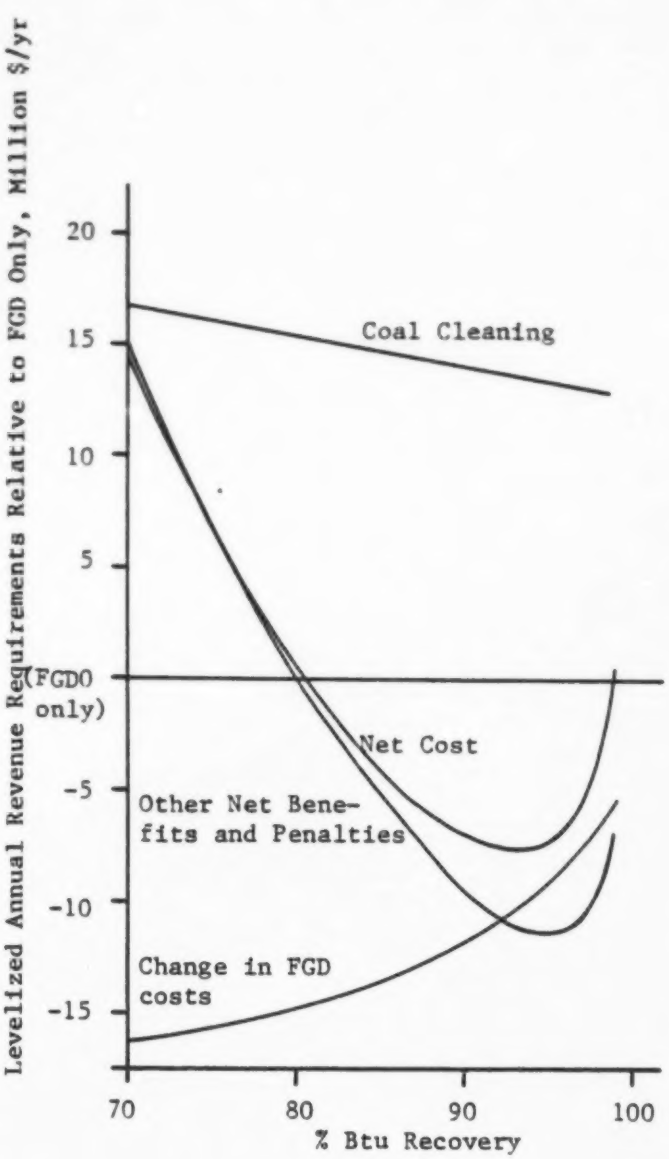


Figure 8. Effect of Btu recovery on the net levelized annual revenue requirements, Pittsburgh coal at 1.20 emission limit.

attributed to the increasing effect of coal lost to the refuse as the Btu recovery decreases. From a further examination of Figure 8, one sees that the combined coal-cleaning/FGD process does have a lower revenue requirement than FGD alone for a certain range of Btu recovery. This is signified by the points along the net cost curve that are less than the zero level, which in this case are from about 80 to 98 percent Btu recovery.

Further comparisons of the curves in Figures 7 and 8 show that each curve has a minimum cost point, but these minima are not located at the same Btu recovery. The curve for the net capital investment has a minimum at about 75 percent Btu recovery, while the net annual revenue requirements curve has a minimum at 93 percent Btu recovery for the Pittsburgh coal.

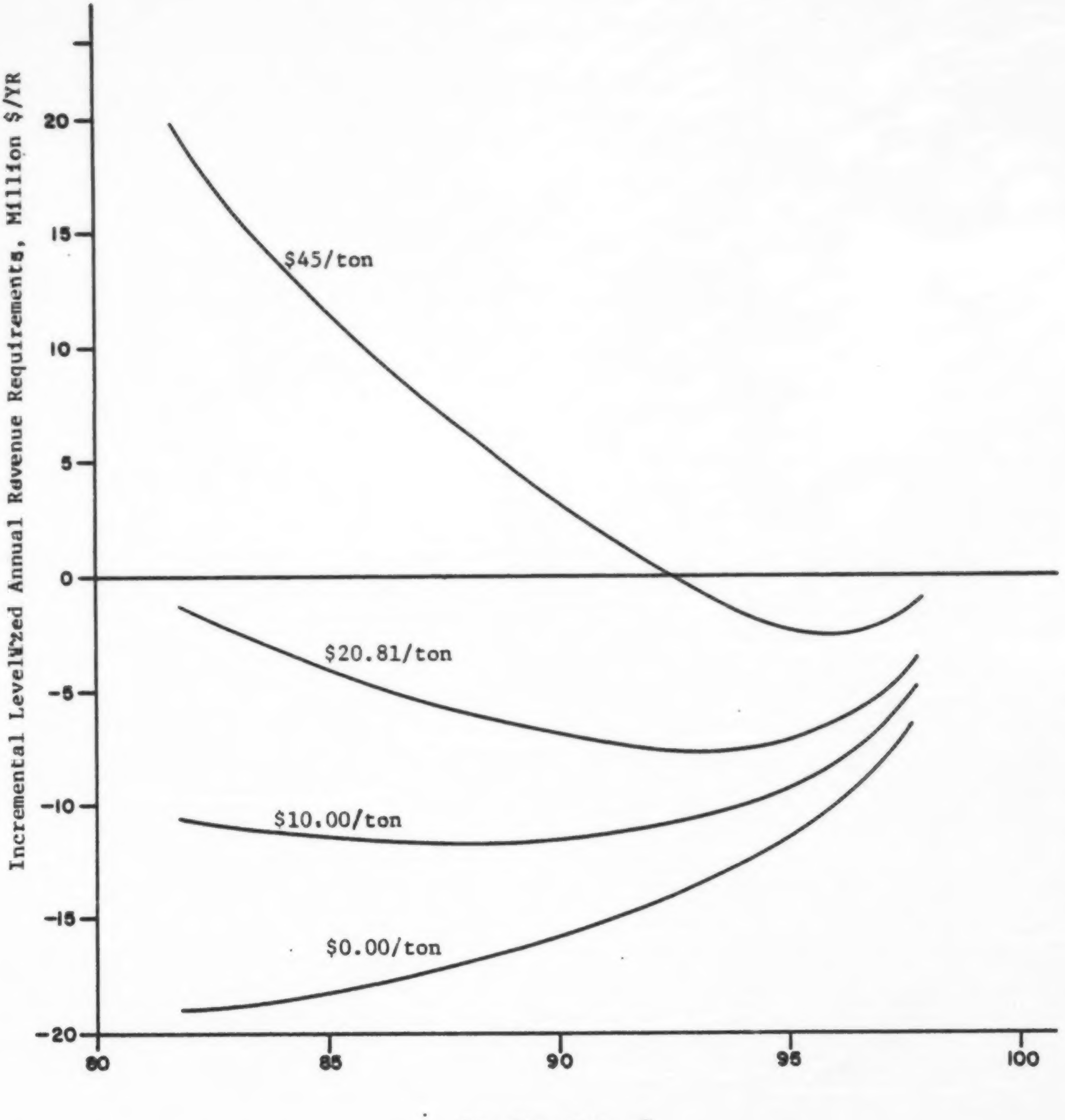
Figure 9 shows the effect of the value assigned to the coal lost to the coal-cleaning plant refuse. One school of thought is that the coal lost during coal cleaning should have a zero value assigned to it since the raw coal may not have a market unless it is cleaned. This is particularly true for coals with high ash contents. The other extreme is to assign full market value to the coal lost. The cost of $20.81 per ton used represents the incremental mining costs associated with mining the increased tonnage of coal, but does not include transportation, UMW pension payments, royalties, sales expenses, and profits. The correct cost to be used in the program is specific to each case. As the value assigned to the coal lost in the refuse increases, this becomes a very significant economic effect.

Figure 10 illustrates the reduction in levelized annual revenue requirements for the four coals at different $SO_2$ emission limits as compared to sulfur removal with FGD alone. Significant differences in levelized annual revenue requirements result from differences in coal washability. Also, the economics generally become more favorable as the $SO_2$ emission limits become less stringent; however, the curves for the Cedar Grove and Upper Freeport coals do have a maximum point beyond which the economics become less favorable. These maxima are located at the points where the optimum pollution control process changes from a combined coal-cleaning/FGD process to a coal-cleaning process, alone. In the cases of the curves for the Illinois No. 6 and Pittsburgh coals, these curves did not reach the point at which coal cleaning could provide the most economical pollution control process without some degree of FGD being necessary.

It should be emphasized that the values assigned to some of the economic benefits and penalties (e.g., boiler availability and maintenance due to burning coal with lower sulfur and ash levels) make significant differences in the economics. While these are based on the best information currently available, some of these relationships have not been fully defined and quantified. Continued work in this area would lead to a better understanding of these relationships.

## PROJECT CONCLUSIONS AND RECOMMENDATIONS

- A computer model capable of calculating the economics of coal-cleaning processes alone and combined with FGD in utility applications has been



Btu Recovery, %

Figure 9. Effect of Btu recovery and unit price charged to coal lost in the refuse on the levelized annual revenue requirements, Pittsburgh coal and 1.2 lb $SO_2$/MBtu emission limit.

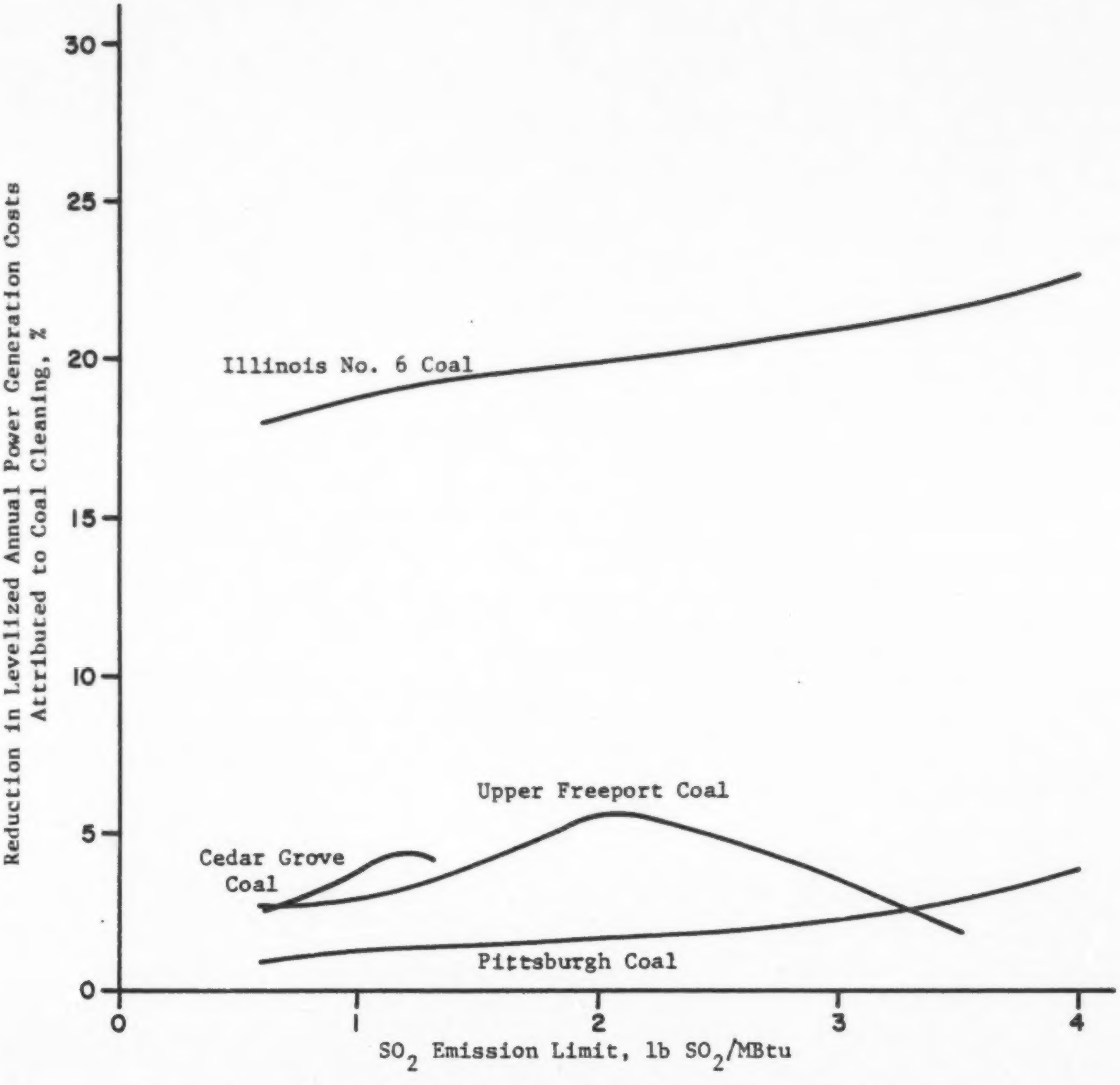


Figure 10. Effect of emission limit on the power generation cost reduction attributable to coal cleaning (at optimum specific gravity).

developed. Selected values from the model agreed closely with values obtained from manual calculations.

- The illustrative runs using four premise coals had coal-cleaning sulfur removals from 14 percent to 57 percent and met some less stringent emission limits without FGD. The combined coal-cleaning/FGD process for each coal had a specific gravity of separation at which costs were at a minimum. Coal cleaning reduced the FGD costs in all cases, primarily by allowing more flue gas to be bypassed. In some cases this reduction in FGD costs offset the costs of coal cleaning. Case-by-case comparisons must be made to determine the most economical approach.

- For the cases studied, it was found that the use of coal cleaning in combination with FGD can have a varied effect on the levelized annual cost of power production. This effect, which is dependent on the coal and the specific operating conditions, ranges from a 0.5 percent increase to a 22.6 percent decrease in those costs.

- The methods used to determine many of the other economic benefits and penalties of coal cleaning are necessarily general in nature because detailed data relating specific coal properties to boiler performance and operating costs are scarce. Thus development and incorporation of more detailed and quantitative data in the model would greatly increase the usefulness of the model in assessing overall economic effects of coal-cleaning. Similarly, the scope of the model could be increased by incorporating other coal-cleaning processes and alternate emission control processes such as fabric filter baghouses and spray dryer FGD and by modifying the functions to allow multiple simultaneous simulations. The economics of retrofit situations should also be considered.

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## CONVERSION FACTORS

| Multiply<br>English Unit | By | To Obtain<br>SI Unit |
|---|---|---|
| pound (lb) | 453.59 | gram (g) |
| ton (2000 lb) | 0.907 | megagram (Mg)<br>= metric ton |
| inch (in.) | 0.0254 | meter (m) |
| foot (ft) | 3.048 | meter (m) |
| British Thermal Unit (Btu) | 1054.88 | Joule (J) |
| Btu/lb | 2.326 | J/g |
| lb/$10^6$ Btu | 429.907 | ng/J |
| $/ton | 1.1025 | $/Mg |
| $/$10^6$ Btu | 0.9480 | mill/MJ =<br>$10^{-3}$\$/MJ |
| lb/ft3 | 0.0160 | g/cm3 |
| mile | 1.609 | km |

Tyler Screen Size Mesh Openings

| Mesh Size | Sieve Opening<br>in. | mm |
|---|---|---|
| 14 | 0.0469 | 1.18 |
| 28 | 0.0234 | 0.60 |
| 48 | 0.0117 | 0.30 |
| 100 | 0.0059 | 0.15 |

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# ECONOMIC EVALUATION OF FGD SYSTEMS

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## ABSTRACT

This paper presents the estimated cost for 17 throwaway and regenerable FGD systems based on December 1982 cost and technology. These systems were also evaluated for operability, technical merit, and commercial availability. The FGD systems were evaluated for high sulfur coal applications at a hypothetical 1000 MW (two 500 MW units) power plant in Kenosha, Wisconsin. This arbitrary reference plant was selected to ensure consistent comparisons, and to increase the relative accuracy of the costs presented.

A flow sheet, material balance, equipment list, system description, and utility consumption list form the basis of each FGD evaluation. Cost information was obtained from process vendors, Stearns-Roger information, and published reports. Capital costs were estimated by factoring costs of process equipment (i.e., an EPRI Class II estimate). Operating costs were estimated from reagent and utility consumption. The levelized capital and operating costs were developed using EPRI's standard economic premises. The costs reported in this study are estimated within an absolute accuracy of ±30 percent. However, since methodology, scope and unit costs are consistent, the relative accuracy between processes is approximately ±15 percent.

## INTRODUCTION

The cost of flue gas desulfurization (FGD) has changed in the last few years due to technological developments, new regulatory requirements, and advances in commercial experience. This paper presents estimated costs for 17 throwaway and regenerable FGD systems based on 1982 costs and technology. These systems were evaluated for operability, technical merit, and commercial availability, and these factors are reflected in the costs presented.

The 17 FGD systems range widely in level of development, from those processes which have received only bench-scale testing to those which have been commercially available for many years. The estimates and evaluations of the commercially available systems (e.g., conventional limestone and Wellman-Lord) provide a reference to which the various processes are compared.

The FGD systems were evaluated for both high and low sulfur coal applications at a hypothetical 1000 MW (two 500 MW units) power plant located in Kenosha, Wisconsin. A specific reference plant was selected to ensure consistent comparisons, and to increase the relative accuracy of the costs presented.

Process vendors, Stearns-Roger, and published reports provide the basis for the estimates and evaluations. Capital costs were estimated by factoring costs of process equipment (i.e., an EPRI Class II factored estimate with an accuracy of ± 15 to 30 percent). Process equipment sizing and costs were developed by Stearns-Roger. Operating costs were calculated based on reagent and utility consumption, operating labor and maintenance requirements. Levelized costs, i.e., the additional cost to produce power as a result of the FGD system, were developed using EPRI's standard economic premises. Costs have an absolute accuracy of ±30 percent. However, since methodology, scope, and unit costs are consistent, the relative accuracy of the estimates is approximately ±15 percent.

Cost and technical evaluations are summarized for each of the 17 FGD processes and are arranged in the following three categories:

- High-sulfur coal--throwaway, where the FGD system is applied to a high-sulfur coal, and the waste product is gypsum or a sludge. Processes in this category include conventional limestone, Chiyoda Thoroughbred 121, Dowa, limestone with forced oxidation, Saarberg-Holter, limestone dual alkali, lime dual alkali, and wet lime.

- High-sulfur coal--regenerable, in which the FGD system is applied to a high sulfur coal and produces a by-product while regenerating the absorbing reagent. Processes in this category include Wellman-Lord, MgO, SULF-X, Flakt-Boliden, aqueous carbonate, and Conosox.

- Low-sulfur coal--throwaway, where the FGD system is applied to a low sulfur coal, and the waste product is a sludge or dry solid. Processes in this category include conventional limestone, lime spray dryer, and nahcolite/trona injection.

## HIGH SULFUR COAL--THROWAWAY

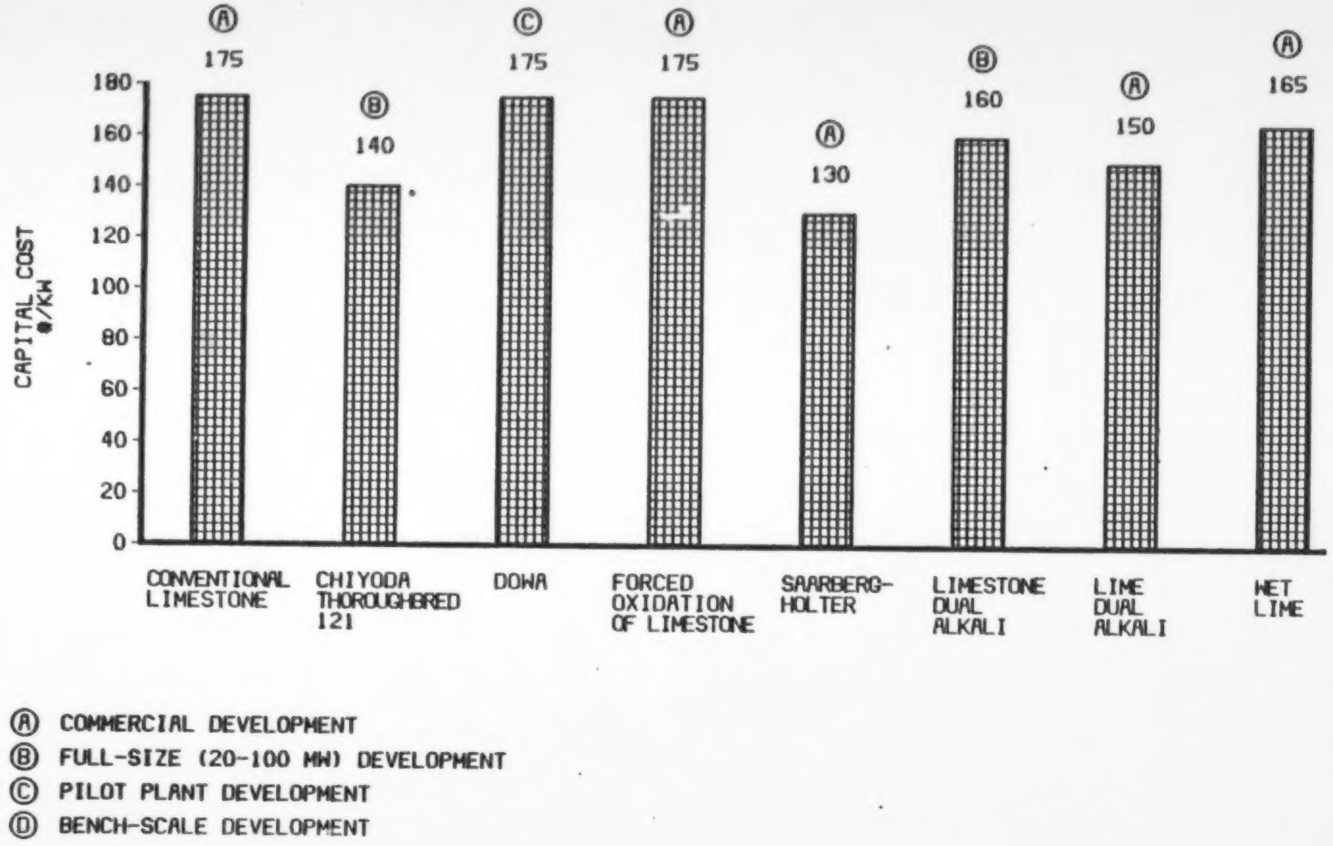
Processes in this category include first generation FGD technologies (conventional limestone and wet lime), and second generation FGD technologies which have the potential for lower operating and capital costs. The conventional limestone process has experienced the broadest application and is considered to be the reference or base case for this category.

Capital and levelized busbar costs are shown in Figures 1 and 2, respectively, with the base case (conventional limestone) process shown at the left. The level of development is also indicated for each process. Figure 2 shows capital, and fixed and variable operating costs which comprise the total levelized busbar cost. The costs exclude particulate removal equipment. It has been assumed that flue gas reheat will be required for all high sulfur, wet FGD systems. This assumption is site specific and should be treated accordingly. The following conclusions can be drawn from Figures 1 and 2:

- The Chiyoda Thoroughbred 121 process has the lowest levelized busbar cost. This is largely due to its low operating cost which results from high limestone utilization, low reagent cost, and low solid waste handling costs.
- The capital cost of the lime dual alkali process is a little less than the other dual alkali processes because of its less costly lime handling and preparation area (versus limestone) and a lower process contingency due to a higher level of development.
- The lime dual alkali process has one of the highest variable operating costs primarily because it uses lime for regeneration.
- The Dowa process has the lowest variable operating cost because it produces a gypsum waste which is less expensive to dispose of than the sludge produced by other processes which do not oxidize the waste solids.

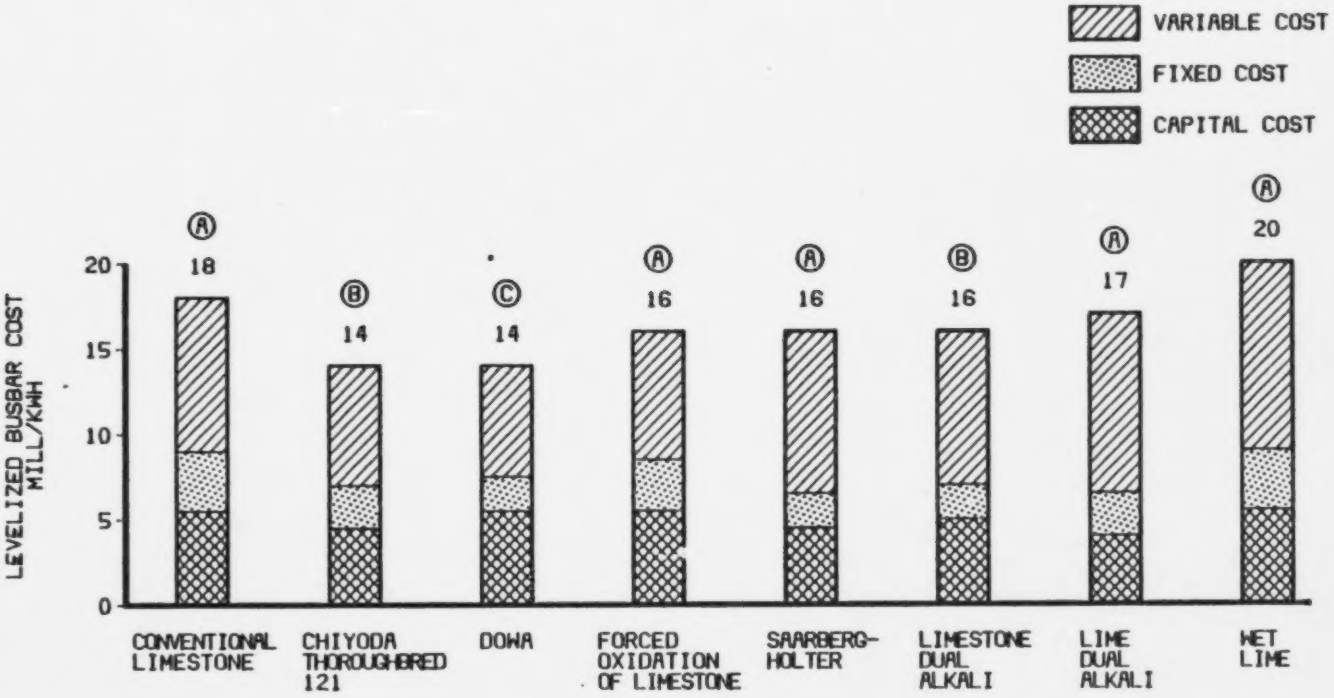
Cost sensitivities to various parameters were developed for each of the high sulfur coal-throwaway processes by adjusting capital and operating costs. The parameters investigated are shown in Table 1 along with the results of the sensitivity analyses.

Cost sensitivities to both zero-inflation and 10-year plant life were also investigated for each process. The zero-inflation parameter reduced system costs to approximately 40 percent of the base case levelized cost. A 10-year plant life was found to reduce process levelized costs to approximately 80 percent of the original base case cost. However, the cost of each process relative to the other processes did not change.



NOTE: COST $/KW IN DEC. 1982 DOLLARS

FIGURE 1. High Sulfur Coal - Throwaway Processes Capital Cost



Ⓐ COMMERCIAL DEVELOPMENT
Ⓑ FULL-SIZE (20-100 MW) DEVELOPMENT
Ⓒ PILOT PLANT DEVELOPMENT
Ⓓ BENCH-SCALE DEVELOPMENT

NOTE: COST LEVELIZED MILL/KWH IN DEC. 1982 DOLLARS

FIGURE 2. High Sulfur Coal - Throwaway Processes Levelized Busbar Cost

TABLE 1. HIGH SULFUR COAL - THROWAWAY PROCESSES COST SENSITIVITY

| SENSITIVITY PARAMETER | CONVENTIONAL LIMESTONE | CHIYODA THOROUGHBRED 121 | DOWA | FORCED OXIDATION OF LIMESTONE | SAARBERG-HOLTER | LIMESTONE DUAL ALKALI | LIME DUAL ALKALI | WET LIME |
|---|---|---|---|---|---|---|---|---|
| % SULFUR IN COAL | *** | *** | *** | *** | *** | *** | *** | *** |
| REAGENT CONSUMPTION/COST | ** | ** | ** | * | * | ** | ** | ** |
| DISPOSAL COST | ** | * | * | * | * | ** | ** | ** |
| POWER COST | ** | ** | ** | ** | ** | ** | ** | ** |
| MAINTENANCE REQUIREMENT | ** | ** | ** | ** | ** | ** | ** | ** |
| ALTITUDE (GAS FLOW) | ** | ** | ** | ** | ** | ** | ** | ** |

*LITTLE OR NO COST SENSITIVITY
**MODERATE COST SENSITIVITY
***HIGH COST SENSITIVITY
****EXTREME COST SENSITIVITY

Sensitivity analyses allow utility personnel to estimate the cost of an FGD system given the site specific conditions. Base case values are defined by General and Process Specific Design Criteria assumed for this study.

A brief summary of each process follows.

### Conventional Limestone (Reference Process)

A limestone slurry solution absorbs $SO_2$ in a spray tower and forms a calcium sulfite/sulfate sludge. The major advantage of this process is its wide range of commercial development and its abundant and low cost absorbent. Also, this process usually will meet the $SO_2$ reduction requirement for all types of coals. This system has the potential disadvantages of equipment scaling, plugging, corrosion, and erosion.

### Chiyoda Thoroughbred 121

This process uses a limestone slurry in a single vessel jet bubbling reactor to remove $SO_2$, oxidize the reaction products, and form calcium sulfate. The major advantages of this second generation process relative to the conventional limestone process are the better settling, filtering, and structural properties of the waste, and better utilization of the limestone. Slurry pumps are not required, reducing capital and maintenance costs. Scaling and plugging problems are reduced because precipitation occurs on recirculated crystals rather than on equipment surfaces. A disadvantage of this process is its low level of development in this country.

### Dowa

An aluminum sulfate solution absorbs $SO_2$ in a packed tower. The spent reagent is oxidized and then regenerated with limestone to form a gypsum product. The major advantages of the Dowa process relative to the conventional limestone process are better settling, filtering, and structural properties of the waste, more efficient use of limestone, and better turndown and load following capabilities. A possible disadvantage is that waste disposal regulations may require a lined waste disposal site because of the soluble aluminum sulfate occluded in the waste. Additionally, this process has a low level of development in this country.

### Forced Oxidation-Limestone

A limestone slurry sprayed into a tower removes $SO_2$ and forms a precipitate of calcium sulfite/sulfate. This waste is subsequently oxidized to form a gypsum product. The major advantages of this process relative to conventional limestone are the better settling, filtering, and structural properties of the waste.

## Saarberg-Holter

A clear alkaline (lime) solution is used in a "Rotopart" scrubber to remove $SO_2$ and form a precipitate of calcium sulfite/sulfate. The calcium sulfite is oxidized within the scrubber vessel to form a gypsum product. The major advantages of this process relative to conventional limestone are virtually 100 percent utilization of the reagent, better settling, filtering, and structural properties of the waste, and better turndown and load following capabilities. This process results in a lower levelized cost than the conventional limestone process even though it uses a more costly reagent. A throwaway FGD process using lime as a reagent requires more potable make-up water than does a throwaway process utilizing limestone; lime slaking requires uncontaminated water. This is a possible disadvantage to the water and wastewater management system.

Some additional observations can be made when comparing oxidized by-product processes to one another. The Saarberg-Holter, Chiyoda Thoroughbred 121, and Forced Oxidation-Limestone processes are similar because they utilize a single loop system to produce a gypsum waste. Oxidation of the calcium sulfite to gypsum is internal to the absorber module in the Saarberg-Holter and Chiyoda Thoroughbred 121 processes and external in the Forced Oxidation-Limestone process. External oxidation increases pumping requirements and results in higher maintenance and fixed costs than the Saarberg-Holter and Chiyoda Thoroughbred 121 processes. The Saarberg-Holter uses lime, which is more expensive than the limestone reagent used in the Chiyoda Thoroughbred 121 and Forced Oxidation-Limestone processes. The use of lime causes the Saarberg-Holter to have a higher variable operating cost than the other two processes. The Chiyoda Thoroughbred 121 is attractive because it has the lowest levelized busbar cost compared to the other two processes. However, it's level of development is less than the commercial Saarberg-Holter and Forced Oxidation-Limestone processes.

## Limestone Dual Alkali

A sodium sulfite solution is used in a spray tower to remove $SO_2$. Limestone is added to the spent solution in a separate loop to simultaneously regenerate the spent solution and form a calcium sulfite/sulfate sludge. The major advantage of this process relative to conventional limestone is lower scaling, plugging, corrosion, and erosion potential which results in higher FGD system availability and lower maintenance requirements. The high reactivity of the sodium reagent allows a lower liquid/gas (L/G) ratio, lower pumping power, and better turndown and load following capabilities than the conventional limestone process. Disadvantages include the possibility that local regulations may require the use of a lined waste disposal site because of the soluble sodium salts occluded in the waste, and low level of development.

## Lime Dual Alkali

Similar to the Limestone Dual Alkali system, a sodium sulfite solution is used in a spray tower to remove $SO_2$. However, lime, rather than limestone, is added to the spent absorbent solution to simultaneously regenerate the sodium sulfite solution and form a calcium sulfite sludge. The major advantages of this process relative to conventional limestone are once again lower scaling, plugging, corrosion, and erosion potential which result in higher availability and lower maintenance requirements. As previously discussed, the sodium reagent allows a lower L/G ratio, lower pumping power consumption, and better turndown and load following capabilities than the conventional limestone process. Local regulations may require the use of a lined waste disposal site because of the soluble sodium salts also occluded in this waste.

The Lime Dual Alkali, Limestone Dual Alkali, and Dowa processes are similar in that they are dual-loop processes. These processes use a clear absorbing solution in the first loop and regenerate the spent absorbent in the second loop (external to the absorber) where the solid wastes are generated. The Dowa process has the lowest levelized busbar cost; however, it has only been tested at the pilot plant level (10 MW). The higher-cost limestone dual alkali process has been demonstrated at a 23 MW facility. The lime dual alkali process has the highest cost; however, it has been operated successfully on a commercial level.

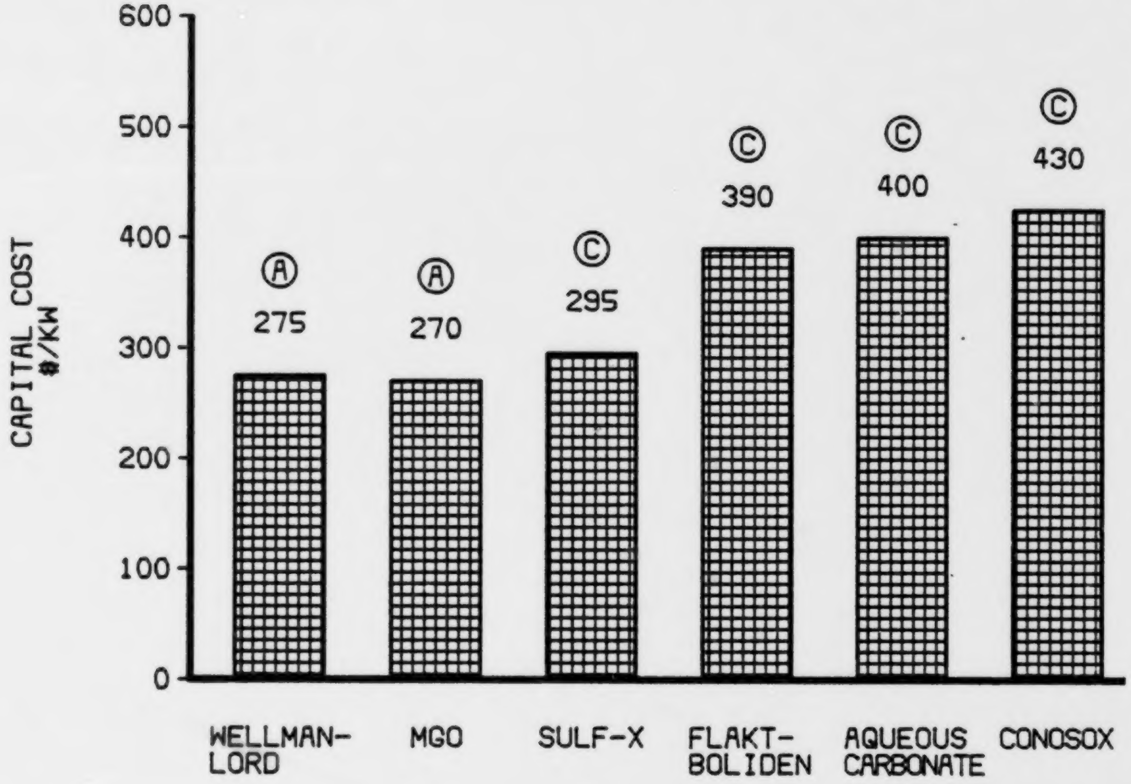
## Wet Lime

A lime slurry solution absorbs $SO_2$ in a spray tower and forms a calcium sulfite/sulfate sludge. The advantages of the Wet Lime process relative to conventional limestone are less erosion, approximately 100 percent use of the reagent, and better turndown and load following capabilities. The major disadvantage is the high cost of lime versus limestone. The lime slurry also requires service water for the slaking process instead of the less expensive cooling tower blowdown water used for limestone slurry preparation.

## HIGH-SULFUR COAL--REGENERABLE WITH BY-PRODUCT

Although processes in this category exhibit higher costs than throwaway processes, by-product regenerable processes are beneficial when space or disposal requirements are restricted and/or when there is an available market for process by-products. The Wellman-Lord process has experienced the broadest application and is considered the basis for comparison with other processes in this category.

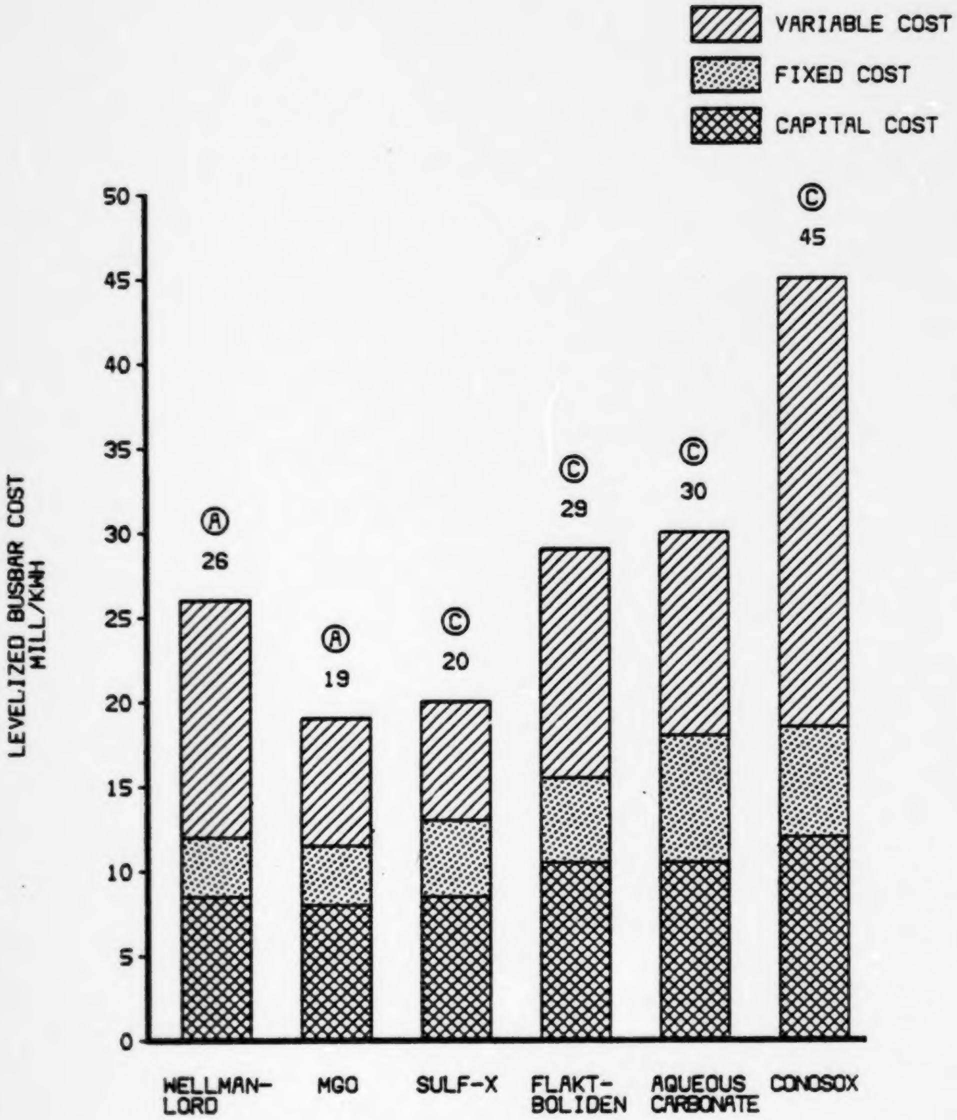
The capital and levelized busbar costs are shown in Figures 3 and 4, respectively, with the base case Wellman-Lord process shown on the left. The level of development is also indicated for each process. Figure 4 shows the capital, fixed, and variable operating costs which comprise the



Ⓐ COMMERCIAL DEVELOPMENT
Ⓑ FULL-SIZE (20-100 MW) DEVELOPMENT
Ⓒ PILOT PLANT DEVELOPMENT
Ⓓ BENCH-SCALE DEVELOPMENT

NOTE: $/KW IN DEC. 1982 DOLLARS

FIGURE 3. High Sulfur Coal - Regenerable Processes Capital Cost



Ⓐ COMMERCIAL DEVELOPMENT
Ⓑ FULL-SIZE (20-100 MW) DEVELOPMENT
Ⓒ PILOT PLANT DEVELOPMENT
Ⓓ BENCH-SCALE DEVELOPMENT

NOTE: LEVELIZED MILL/KWH IN DEC. 1982 DOLLARS

FIGURE 4. High Sulfur Coal - Regenerable Processes Levelized Busbar Cost

total levelized busbar cost. It has been assumed that flue gas reheat will be required for all high sulfur, wet FGD systems (this does not include the spray dryer based Aqueous Carbonate process). This assumption is site specific and should be treated accordingly.

An economic evaluation of these regenerable FGD processes resulted in the following major conclusions:

- The MgO process has the lowest levelized cost but is very sensitive to sulfuric acid by-product credit. This recovery process carries the lowest capital cost of all the recovery processes.

- The Sulf-X process has a slightly higher levelized cost than has the MgO process but has the advantage of possibly reducing $NO_x$ emissions simultaneously. This process does not have a high level of development.

- Some of the other regenerable processes, notably the Wellman-Lord and Flakt FGD systems, produce a concentrated $SO_2$ stream which could be used for sulfuric acid production. However, for the purposes of this evaluation, these processes were combined with an Allied Chemical/Claus sulfur plant to produce elemental sulfur. The levelized costs for both these processes would be lower if they were combined with a sulfuric acid plant. Producing sulfuric acid product avoids the need to purchase high-cost methane and provides (presently) for a more valuable by-product.

Cost sensitivities to various parameters were developed for each process by adjusting the capital and operating cost. These parameters are shown in Table 2 along with the relative results. The cost sensitivity analyses to both zero-inflation and 10-year plant life were found to have no significant impact on the relative costs between the regenerable processes. This result was discussed previously in the High Sulfur-Throwaway section. Once again, sensitivity analyses allow utility personnel to estimate the cost of an FGD system given the site specific conditions.

Wellman-Lord (Reference system to which other regenerable processes are compared)

A concentrated solution of sodium sulfite is used in a tray tower to produce a sodium bisulfite-rich solution. This solution is thermally regenerated to sodium sulfite in a steam evaporator and a concentrated $SO_2$ gas stream is produced. The $SO_2$ is subsequently converted to sulfur in an Allied Chemical plant. The Wellman-Lord process has the advantages of producing a salable by-product and does not experience scaling or plugging. Disadvantages include high operating costs because of the large quantities of low pressure steam and methane required and high capital costs. Additionally, the Wellman-Lord process is sensitive to flue gas particulates, HCl and $SO_3$ and therefore requires a prescrubber. A prescrubber results in higher operating costs due to higher pressure drop and prescrubber loop blowdown treatment.

## MgO

A magnesium oxide solution is sprayed into a grid-packed tower to remove $SO_2$ and form magnesium sulfite/sulfate. A calcining operation regenerates the waste solids to magnesium oxide and forms an $SO_2$ gas. The $SO_2$ gas is subsequently processed to produce sulfuric acid. The advantage of this process relative to the Wellman-Lord process is much lower operating cost. This is due to steam production during the calcination step, whereas the Wellman-Lord process consumes large quantities of steam. The disadvantages of the MgO process include a higher reagent makeup requirement due to a high oxidation rate, use of a high temperature (1800°F) calciner, potential pluggage of the gas/solid separation equipment at the calciner outlet, and corrosion/erosion problems in the slurry handling equipment.

TABLE 2. HIGH SULFUR COAL - REGENERABLE PROCESSES COST SENSITIVITY

| SENSITIVITY PARAMETER | WELLMAN-LORD | MGO | SULF-X | FLAKT-BOLIDEN | AQUEOUS CARBONATE | CONSOX |
|---|---|---|---|---|---|---|
| % SULFUR IN COAL | ••• | •• | •• | •• | •• | •••• |
| REAGENT CONSUMPTION/COST | • | •• | • | •• | •• | •• |
| BY PRODUCT VALUE | •• | ••• | •• | •• | •• | •• |
| POWER COST | •• | •• | •• | •• | •• | • |
| MAINTENANCE REQUIREMENT | •• | •• | •• | •• | •• | •• |
| ALTITUDE (GAS FLOW) | • | • | • | • | • | • |

•LITTLE OR NO COST SENSITIVITY
••MODERATE COST SENSITIVITY
•••HIGH COST SENSITIVITY
••••EXTREME COST SENSITIVITY

## Sulf-X

An iron sulfide slurry passes through a packed tower removing $SO_2$ from the flue gas. The spent absorbent is regenerated in a calciner, producing an elemental sulfur off-gas which is condensed to form liquid sulfur. The advantages of the Sulf-X process relative to the Wellman-Lord process are a low oxidation rate which results in a lower reagent make-up requirement, potential for simultaneous $NO_x$ removal, and low fuel consumption. Disadvantages of the Sulf-X process include: possible release of $H_2S$ gas in the absorber during an upset; handling of three reagents (pyrites, coke, and sodium sulfide) which increases material handling; slurry absorption which increases the potential for equipment erosion; high temperatures required in the kiln increase the potential for process control problems and equipment failures; and low level of development.

## Flakt-Boliden

A sodium citrate solution flows downward (countercurrent to the flue gas) through a packed tower to remove $SO_2$. The spent absorbent solution is regenerated in a stripper column while producing an $SO_2$ rich gas stream, which is converted to sulfur in an Allied Chemical/Claus plant. The advantage of the Flakt-Boliden process relative to the Wellman-Lord process is its lower oxidation rate, which results in a lower reagent consumption rate. The vacuum crystallization process used in the sulfate-purge system is a disadvantage in the Flakt-Boliden process because it is more difficult to control than the thermal crystallization system in the Wellman-Lord process.

## Aqueous Carbonate

A solution of sodium carbonate absorbs $SO_2$ in a spray dryer. The waste product from the spray dryer is treated using a coke reductant in a molten-salt bed to regenerate the scrubbing reagent while producing a hydrogen sulfide-rich gas. The hydrogen sulfide is converted to sulfur in a Claus plant. The major advantages of the aqueous carbonate process relative to the Wellman-Lord process are a lower steam consumption rate and insensitivity to oxidation in the absorber. Disadvantages result from the complexity of the operation, handling two phase flow and high equipment operating temperatures. Additionally, the sodium reagent and fly ash may tend to accumulate on the spray dryer walls, reducing absorption efficiency; also the crystallizer and carbonator are susceptible to plugging due to the formation of bicarbonate crystals. This process is at the demonstration stage of development.

## Conosox

A solution of potassium salts is used to remove $SO_2$ in a packed tower. The spent potassium bisulfite absorbent is converted to a potassium thiosulfate solution, which is in turn reduced with carbon monoxide to yield regenerated potassium carbonate and hydrogen sulfide gas. The hydrogen sulfide gas is subsequently converted to sulfur in a Claus plant. The major advantages of the Conosox process relative to the Wellman-Lord process are the use of a more reactive reagent (potassium vs. sodium), lower oxidation rate (i.e., lower reagent consumption), lower steam consumption, and a low pressure drop across the absorber. Disadvantages of the Conosox process are the use of high temperatures, high pressure vessels, high consumption of fuel and liquid oxygen, and the potential for release of hydrogen sulfide gas in the absorber.

## LOW-SULFUR COAL--THROWAWAY

Included in this category are lime spray drying, dry injection of nahcolite/trona, and the conventional limestone slurry scrubbers. The conventional limestone process has experienced the broadest application and is considered as the basis for comparison in this category.

The capital and levelized busbar costs are shown in Figures 5 and 6, respectively, with the base case (conventional limestone) process shown at the left. The level of development is also indicated for each process. Figure 6 shows the capital, and fixed and variable operating costs which comprise the total levelized busbar cost. The costs exclude particulate removal equipment.

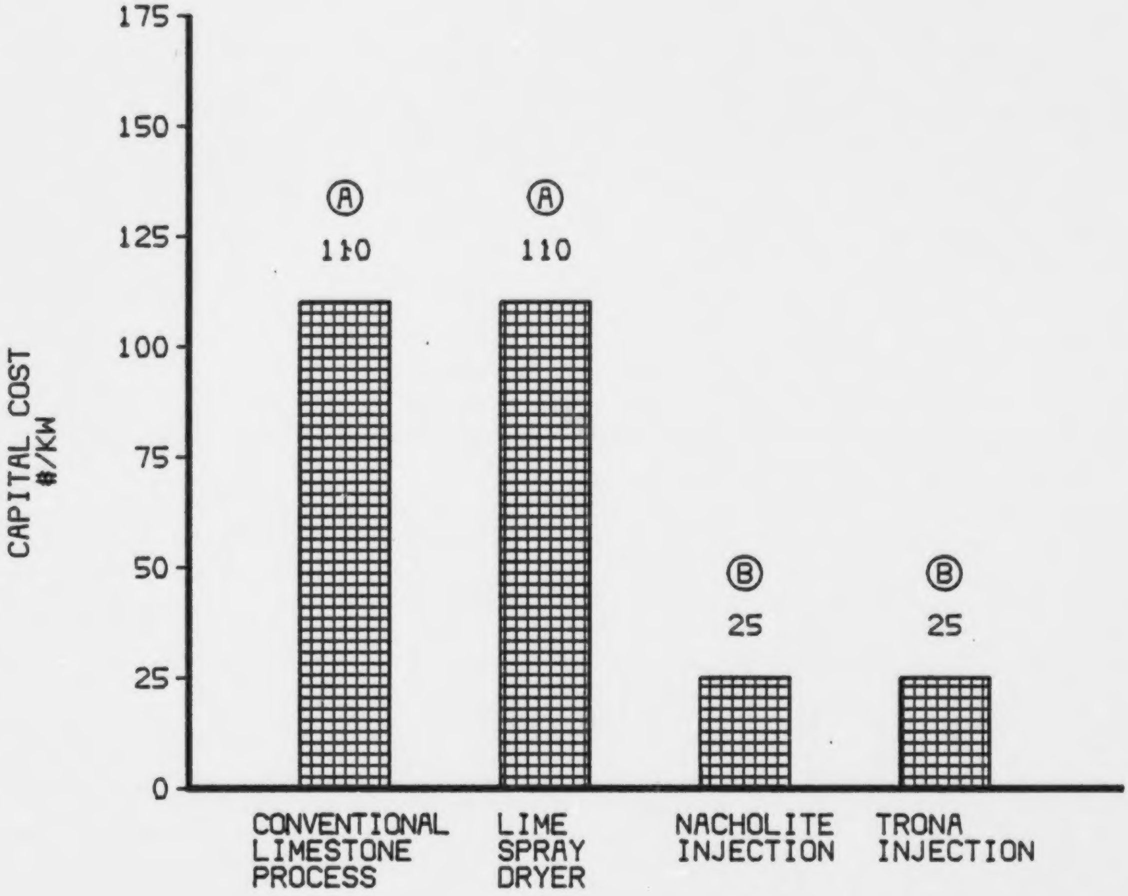
The following conclusions can be drawn from Figures 5 and 6:

- The Trona Injection process has the lowest levelized cost resulting from very low capital and fixed operating costs. The high variable operating cost due to consumption of expensive reagents offset the former cost advantages substantially.

- The Lime Spray Dryer has a low operating cost due to a combination of factors: low consumption of relatively expensive lime reagent (compared to limestone) due to the low sulfur coal, low waste disposal costs due to the dry waste product, and low energy requirements.

- Nahcolite operating cost exceeds both spray drying and trona injection. However, the operating cost is very sensitive to the assumed nahcolite cost which is 140 $/ton in this evaluation. Other EPRI reports have based their evaluations on lower nahcolite costs ranging between $50-100/ton delivered which reduced the operating cost significantly. This range was selected based on more recent reagent cost data from suppliers using solution mining methods and on transportation costs for sodium-based compounds shipped throughout the U.S.

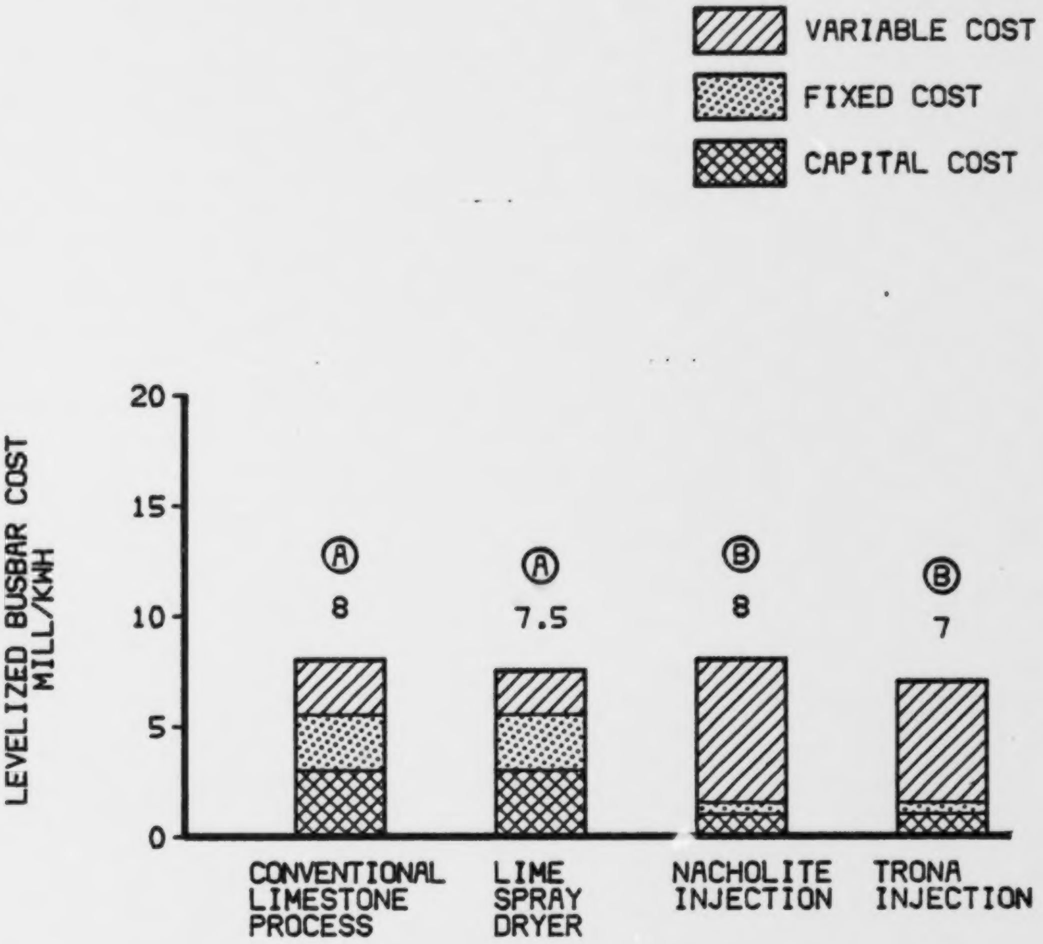
The cost sensitivities for each of the processes were developed by adjusting the capital and operating cost in accordance with various parameters. The parameters investigated for their effect on cost are shown in Table 3 along with the results.



Ⓐ COMMERCIAL DEVELOPMENT
Ⓑ FULL-SIZE (20-100 MW) DEVELOPMENT
Ⓒ PILOT PLANT DEVELOPMENT
Ⓓ BENCH-SCALE DEVELOPMENT

NOTE: COST $/KW IN DEC. 1982 DOLLARS

FIGURE 5. Low Sulfur Coal - Throwaway Processes Capital Cost



Ⓐ COMMERCIAL DEVELOPMENT
Ⓑ FULL-SIZE (20-100 MW) DEVELOPMENT
Ⓒ PILOT PLANT DEVELOPMENT
Ⓓ BENCH-SCALE DEVELOPMENT

NOTE: 30 YR. LEVELIZED COST MILL/KWH IN DEC. 1982 DOLLARS

FIGURE 6. Low Sulfur Coal - Throwaway Processes Levelized Busbar Cost

TABLE 3. LOW SULFUR COAL - THROWAWAY PROCESSES COST SENSITIVITY

| SENSITIVITY PARAMETER | LIME SPRAY DRYER | NACHOLITE INJECTION |
|---|---|---|
| % SULFUR IN COAL | •• | •••• |
| REAGENT CONSUMPTION/COST | •• | •••• |
| DISPOSAL COST | • | • |
| POWER COST | •• | • |
| MAINTENANCE REQUIREMENT | • | •• |
| ALTITUDE (GAS FLOW) | •• | • |

*LITTLE OR NO COST SENSITIVITY
**MODERATE COST SENSITIVITY
***HIGH COST SENSITIVITY
****EXTREME COST SENSITIVITY

### Conventional Limestone (Reference System)

This process is identical to that described in the conventional limestone discussion under high-sulfur--throwaway processes, but differs in that it has been evaluated for a low sulfur coal application requiring only 70 percent $SO_2$ removal.

### Lime Spray Dryer

The lime spray dryer process contacts flue gas with lime slurry in a spray dryer to produce a dry waste. The slurry reacts with $SO_2$ to form a solid which is collected in a baghouse with the fly ash. Relative to the conventional limestone process, the advantages of this process are dry waste handling, lower maintenance requirements, lower energy requirements, and lower capital and operating costs. Disadvantages include the potential to "blind" the baghouse bags during process upsets, and the potential for scale formation in the spray dryer.

### Nahcolite Injection

In this process nahcolite (sodium bicarbonate) is pulverized and injected into the flue gas duct to react with $SO_2$. The dry waste is removed in a baghouse. The advantages of nahcolite injection relative to the conventional limestone process are dry waste handling, lower maintenance requirements, reduced energy requirements, and lower capital and operating costs. Disadvantages include increased reagent use below 275°F flue gas temperature, lack of a reagent supplier, the possibility of local regulations requiring the use of a lined waste disposal site because of the soluble sodium salts in the waste, and high sensitivity to largely unknown reagent cost. The cost of nahcolite was estimated at $140/t which was obtained from the trona mining industry. However, nahcolite has never been mined commercially and the cost is very uncertain (see the conclusions summarized previously). Nahcolite injection is best suited to locations near the reagent source in Colorado and in dry regions where waste disposal is less of a problem.

### Trona Injection

The pulverization and injection of trona (sodium bicarbonate plus sodium carbonate) into the flue gas was investigated as an alternative to nahcolite injection. Trona is currently less expensive than nahcolite and is commercially available. The lower cost of trona results in a variable operating cost of 6 mills/kWh versus 7 mills/kWh with nahcolite. The capital and fixed cost of the trona injection system are the same as that of nahcolite. The levelized busbar cost of the trona injection system is the lowest in this category; however, its level of development is lower than the commercial lime spray dryer and the conventional limestone process.

# ESTIMATING PROCEDURE FOR RETROFIT FGD COSTS

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## ABSTRACT

A procedure has been developed for utility engineers to estimate site-specific flue gas desulfurization (FGD) retrofit costs on existing power plants. This procedure has been developed for six FGD processes: limestone, lime, dual alkali, lime spray dryer, wallboard gypsum, Wellman-Lord, and Chiyoda. Economic results from the calculation procedure include capital cost, operating and maintenance (O&M) costs, levelized cost, and cost per ton of sulfur dioxide removed.

## INTRODUCTION

Previous studies have estimated the incremental cost of an FGD system on a new power plant; however, limited information is available concerning the cost of an FGD system retrofitted to an existing plant. Many utility engineers estimate retrofit FGD capital cost for a specific existing plant using an average "retrofit factor" of 1.3 as a guide. Stearns-Roger, under EPRI sponsorship, has developed a method to more accurately estimate FGD retrofit costs. A report, entitled "Retrofit FGD Estimating Guidelines," will be published in mid-1984.

The procedures outlined in this study consider major factors which affect FGD capital costs at a particular site such as chimney modifications, space availability, demolition and relocation of existing equipment, underground obstructions, soil conditions, local labor rates, degree of site congestion, and accessibility of the site for construction. Several process-related items also are considered, including percent sulfur in coal, percent $SO_2$ removal, plant size, flue gas flow rate, and gas reheat requirements.

The calculation methods described in this study should apply to over 90% of FGD retrofit situations. When all the retrofit items previously mentioned are totalled, retrofit FGD costs can range from 10 percent to 100 percent greater than an FGD system on a new plant. The FGD retrofit costs developed through use of this method are sufficient for budget and preliminary planning purposes, but they do not replace the need for more detailed engineering.

The method outlined in this paper establishes a procedure for estimating FGD retrofit costs, but does not provide guidance for selecting the best option or combination of options (i.e., coal cleaning vs. FGD). FGD, one of the more effective $SO_2$ removal techniques, is also one of the more costly compliance options. Therefore, accurate FGD economics are a key issue affecting compliance strategies. FGD also is one of the more difficult options to estimate due to specifics of retrofit constraints, site characteristics, space availability, and type of FGD process selected.

## DISCUSSION OF ESTIMATING PROCEDURE

The basis for economic evaluations in this paper is the capital cost of a new plant FGD system developed in a previous EPRI study, "Economic Evaluation of FGD Systems," CS-3342. This report evaluates FGD costs for a new plant having two (2) 500 MW units, located in Kenosha, WI, burning a 4 percent sulfur coal, designed for 90 percent $SO_2$ removal efficiency, zero bypass, and 50°F indirect steam reheat. The detailed retrofit estimating method is intended specifically for application to the costs developed in CS-3342; however, the estimating method can be applied to new plant costs from any source.

Once the new plant FGD costs are determined, adjustments are made for scope, process, location, and retrofit differences from the base case new plant. Figure 1 outlines the procedure used to adjust the base new plant FGD cost and to determine retrofit cost. The resultant retrofit factors can be applied to cost data from other sources, but this alternate cost data must be based on the same system scope.

### SCOPE ADJUSTMENTS

FGD retrofit construction may require work not necessary for a new plant FGD system. An example would be the addition of an acid resistant chimney downstream of the scrubber or reinforcing a boiler to withstand the higher draft potential. Inclusion of these additional costs in the new plant FGD cost provide a more accurate assessment of the total retrofit impact.

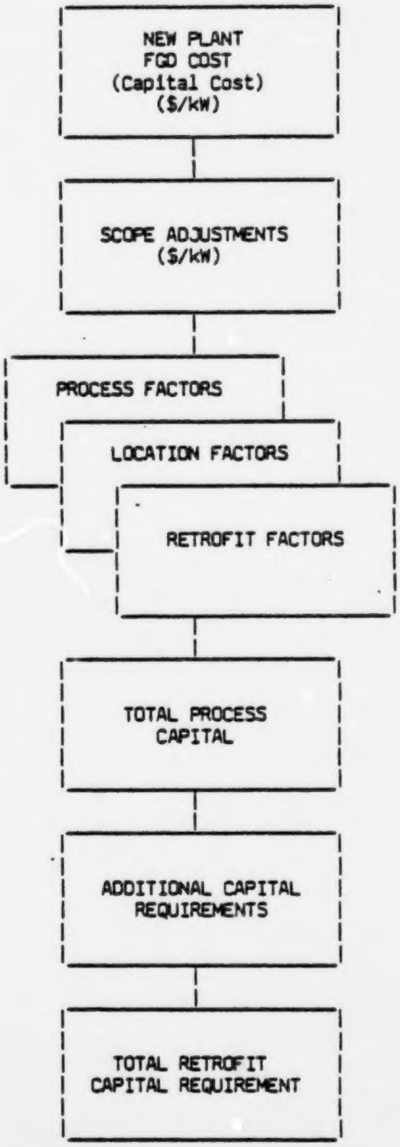

Figure 1. Logic Diagram - Total Retrofit FGD Capital Requirement

Scope adjustments are defined as additional equipment required for a particular FGD retrofit, which would not normally be required for an FGD system on a new power plant. New plant FGD costs should include the following equipment:

- $SO_2$ removal absorber tower
- Duct work and structural support steel from the Induced Draft (I.D.) Fan outlets to the scrubber and from the scrubber outlet to the chimney
- Incremental I.D. fan capacity which provide sufficient draft to overcome the pressure loss in the scrubber
- Reagent feed equipment, including unloading and storage, conveying, and reagent preparation equipment
- Waste handling, including the primary and secondary dewatering equipment as well as sludge fixation equipment, if required
- General support equipment, which includes makeup and seal water tanks and pumps, and an instrument air system

Scope adjustments include any additional equipment costs due to the addition of a scrubber and not included in the equipment areas defined in the previous paragraph. The cost adjustments can contribute an additional 10 percent to a retrofit FGD system's capital cost. The following areas are potential scope adjustments:

- A new chimney, or protection of the existing chimney against the acidic effects of a wet scrubber, including application of linings or pressurization of the annular space
- Structural reinforcement of the boiler to provide negative pressure surge protection, or a draft control system to prevent surges in the boiler
- Any demolition and/or equipment relocation necessary to provide space for the new equipment, such as building removal or cable tray rerouting to allow construction of the FGD system

## PROCESS ADJUSTMENTS

The second adjustment in Figure 1 is the modification of the new plant cost for process differences from the base case. These might include the following:

- Unit size, MW
- Gas flow, ACFM per MW
- Percent sulfur in coal
- $SO_2$ removal efficiency
- Required reheat

With these process adjustments, the user is able to modify the costs for plant capacities ranging from 100 MW up to 700 MW, flue gas flow rate from 2400 to 5300 ACFM/MW, sulfur content from 1 to 6 percent, scrubber removal efficiencies from 50 to 90 percent, and up to a 50°F reheat requirement.

## LOCATION ADJUSTMENTS

The next step is the development of site-specific factors which allow the user to adjust the cost from its base of Kenosha, Wisconsin to any other location. Location adjustments consider the cost effects of the following:

- Seismic Zone - Additional process equipment and engineering costs were calculated based on Unified Building Code Seismic Risk Zones, using historical data from previously constructed plants.
- Climate - Locations warmer than Kenosha, Wisconsin may require less freeze protection equipment, resulting in potential credits for retrofit installations.
- Local Material and Labor Cost - Equipment costs, labor rates, and labor productivity factors were calculated using Means 1983 City Cost indices and other published sources.
- Soil Conditions - Costs for earthwork and foundation construction depend on the soil characteristics; costs for various soil types were calculated using data from previous Stearns-Roger installations.

The most significant of these parameters is local material and labor cost, which can change the actual installed capital cost by as much as 30 percent.

## RETROFIT ADJUSTMENTS

Retrofit adjustments consider the retrofit difficulty which is defined by the following additional site-specific items:

- Access and congestion
- Underground obstructions
- Ductwork tie-in distances
- Distance between the scrubber and waste handling

Site accessibility, area availability and congestion are some of the most serious problems facing any retrofit installation. A severely limited plant site may require location of FGD equipment at some distance from the boiler, which will necessitate long runs of ductwork and piping, increased pumping costs, etc. Elevated construction will also increase the cost of engineering and installation. Poor access to a construction site limits the ability of large cranes to move materials, increasing costs. Finally, congestion may limit crew work space and affect the design and layout of piping, ductwork, etc. The resulting lost productivity and unusual design requirements can significantly increase the total capital requirement for the FGD retrofit.

Underground obstructions are defined as those items which cannot be removed because of logistics, economic considerations, or service requirements. They may include circulating water pipes, gas mains, and duct banks. The cost impacts of these interferences are calculated for each equipment area, based on the degree of difficulty these obstructions would add to the equipment installations. The resulting retrofit factors can then be tabulated for each FGD process.

The distance between the scrubber and the plant tie-in point, and then from the scrubber to the chimney can significantly affect the total retrofit capital cost. Every linear foot of additional ductwork will increase the installed cost of the FGD retrofit above the new plant FGD ductwork design.

The final site-specific retrofit adjustment considers the distance required between the scrubber and the waste disposal and handling system. This increase in piping distance to the primary and secondary dewatering systems can add significantly to the installed FGD retrofit capital requirement.

Access, congestion, and the ductwork distance are the major contributors to the retrofit adjustment. Accessibility and congestion can increase the retrofit cost of any particular system by 50 percent. The retrofit adjustments have the largest effect on the FGD capital cost. These factors can increase capital cost by 70 percent, depending on the degree of retrofit difficulty.

## TOTAL RETROFIT CAPITAL REQUIREMENT

The four adjustment factors applied to the new FGD system cost yield the total process cost (TPC). The total process capital is the constructed cost of on-site FGD and related equipment, plus direct and indirect construction costs. These additional costs must be calculated by factoring the TPC to derive the total retrofit capital requirement. These costs include the following:

- Engineering - Fees for hours spent by equipment supplier, architect-engineer and the utility to finish the installation and FGD system startup.
- Escalation to the date of construction - Cost increases due to equipment price increases after the base case construction date of December, 1982.
- Cost of general support facilities - Including roads, offices, laboratories, fences, etc. which need to be built or reconstructed.
- Allowance for funds during construction - Those charges which accumulate annually as equipment is purchased and installed, prior to plant startup.
- Royalty allowance - The additional fee paid to the process vendor for the use of a proprietary system design.
- Preproduction costs - Intended to cover the operator training, equipment checkout, extra maintenance, and inefficient use of materials during startup.
- Reagent inventory capital - Covers the value of raw materials and other consumables as an initial capital expenditure.

The summation of these costs and the TPC provides the total retrofit capital requirement for the FGD system. If only capital costs are required, the evaluation is complete; however, if the levelized busbar cost is desired, additional calculations are required. These steps are shown in Figure 2.

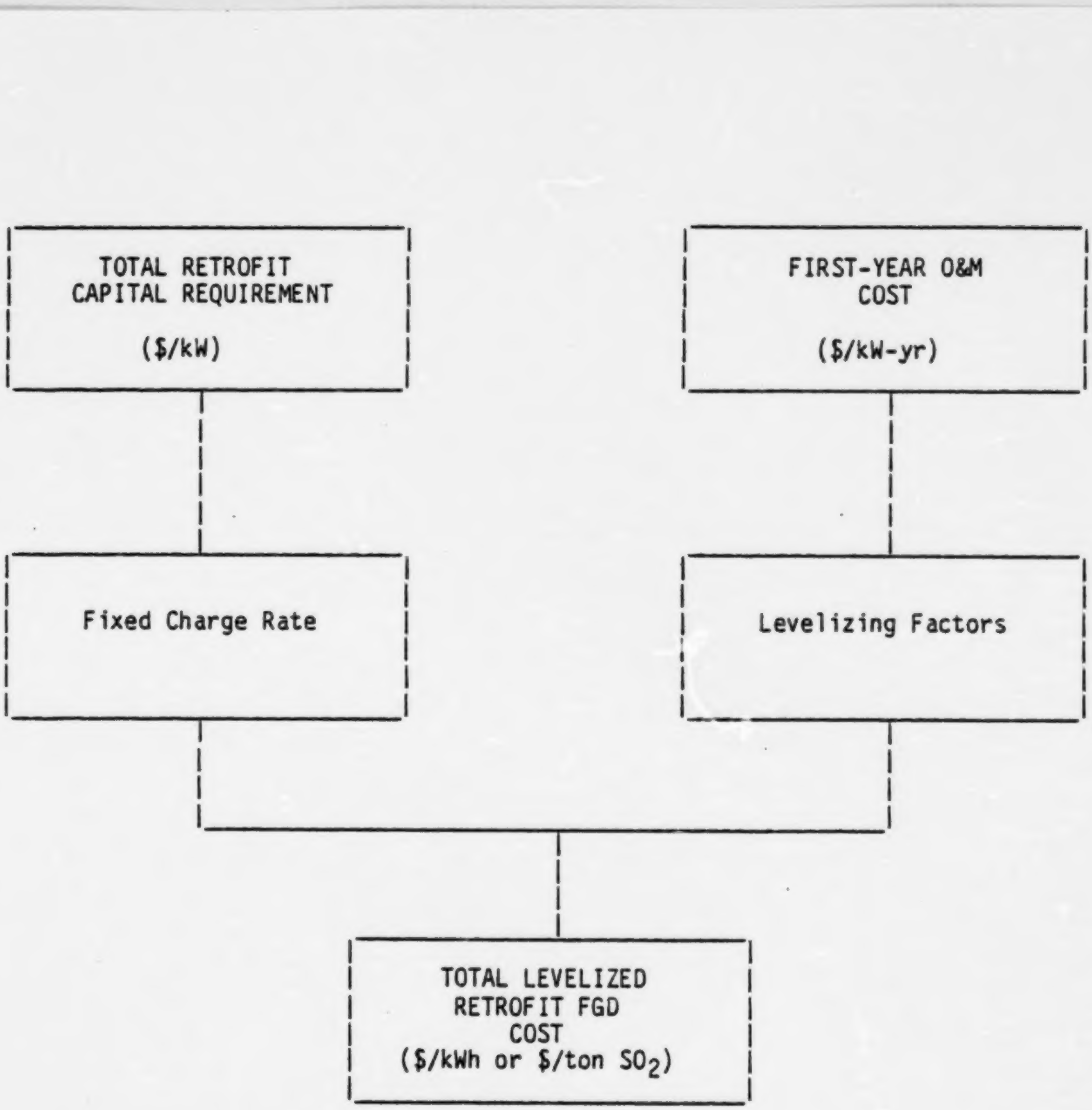
TOTAL RETROFIT CAPITAL REQUIREMENT ($/kW)
FIRST-YEAR O&M COST ($/kW-yr)
Fixed Charge Rate
Levelizing Factors
TOTAL LEVELIZED RETROFIT FGD COST ($/kWh or $/ton $SO_2$)

Figure 2. Logic Diagram - Total Levelized Retrofit FGD Cost

## OPERATING AND MAINTENANCE COSTS

The levelized busbar cost, in mills/kWh or $/ton of $SO_2$ removed, is computed by applying a two-step levelizing procedure. The fixed charge rate when multiplied by the capital cost produces a levelized capital cost over the projected FGD plant life. Levelization factors are applied to the first-year O&M costs to yield a levelized operating cost. These levelization factors are based on the economic premises defined by one's own company. They assume a specific expected inflation rate and discount rate over the life of the plant. O&M costs for the wet limestone system include the following:

- Fixed costs:

  --O&M personnel
  --Maintenance material
  --Administration and support personnel

- Variable costs:

  --Power
  --Reagent
  --Steam usage
  --Waste disposal cost
  --Water consumption

Adding the levelized capital cost to the levelized operating cost results in the total levelized busbar cost for the FGD system.

## LEVELIZED COST

As noted, the retrofit capital and O&M costs are levelized by applying the proper fixed charge rate and levelization factor. These economic factors consider the interest rate, remaining plant life, capacity factors, reagent costs, utility cost, and sludge disposal cost. As the remaining plant life decreases, the fixed charge rate increases and the levelization factor decreases. Therefore, the fixed charge rate will cause the levelized capital cost to increase as the remaining plant life decreases. Levelization factors applied to the O&M cost cause the levelized costs to decrease as the remaining plant life decreases.

## SAMPLE RETROFIT ESTIMATING WORKSHEETS

The retrofit estimating procedure is illustrated in Tables 1 through 3. Only the detailed retrofit cost estimating worksheets are presented. The tables and graphs needed to complete these forms will be published in the final report.

Table 1, the Total Retrofit Capital Estimate Summary, is an example of the procedure used to estimate the total capital requirement for a wet limestone FGD system. In this table, the FGD system capital costs are divided into process areas. Factors are developed for each process area and each cost correction required. Multiplying these factors and summing the retrofit cost yields the total process capital. Economic factors are then calculated from and added to the Total Process Capital to obtain the total retrofit capital requirement. The factors developed for Table 1 are based on Stearns-Roger historical plant cost data and an assessment of retrofit impacts.

Following Table 1 are examples of figures and tables (provided in the final report) which will allow the user to determine the adjustment factors previously discussed in this paper. Table 2 is an example of the location dependent adjustments, in this case the effect of soil on plant cost. For example, a soil with poor bearing capacity, shallow bedrock, and ground water would require five times the foundation cost that dense insitu soils, having a bearing capacity of 4 ksf and over, would require. The foundation cost may represent only 1 percent of the installed equipment cost. Therefore the overall effect of a 500 percent increase in the foundation cost is a 5 percent increase in the total capital requirement.

Figure 3 provides an example of the graphical presentation of unit specific scope adjustments. This example allows calculation of the cost of a chimney addition based on the flue gas flow rate to the absorber.

Once these cost factors are determined and the total capital requirement calculated, the first-year O&M cost must be derived. The first-year O&M costs are divided into fixed and variable costs. Fixed costs calculated for the retrofit estimating procedures are based on EPRI standards and are determined by factoring the equipment cost. The factors and equations necessary to determine these costs will be included in the final report.

The variable O&M cost is calculated for each retrofit situation. The user can calculate variable costs for power, reagent usage, steam, waste disposal, and water within two hours using the questions, tables, and graphs presented in the soon-to-be published study.

Table 3, the First-Year O&M Summation Sheet, is used to tabulate and sum the individual costs; this yields the total fixed and variable first-year O&M cost. The results of Table 3 serve as the basis for determination of the levelized busbar cost. The levelized capital cost and first-year O&M cost are calculated by applying the fixed charge rate and levelization factors respectively.

The final report will provide the figures which graphically illustrate the fixed charge rate (FCR) and levelization factors as a function of remaining life of the plant. By applying these factors and the appropriate conversion constraints, the user can determine the levelized busbar cost in mills/kWh or \$/ton $SO_2$ removed.

## TABLE 1. TOTAL RETROFIT CAPITAL COST ESTIMATE SUMMARY

| Process Area Description | Base Process* Cost $/kW | | Process Factors | | Location Factors | | Retrofit Factors | | Retrofit Cost $/kW |
|---|---|---|---|---|---|---|---|---|---|
| Reagent Feed | 23.0 | x | (_____) | x | (_____) | x | (_____) | = | ______ |
| $SO_2$ Removal | 78.0 | x | (_____) | x | (_____) | x | (_____) | = | ______ |
| Flue Gas Handling | 30.0 | x | (_____) | x | (_____) | x | (_____) | = | ______ |
| Waste Handling | 23.6 | x | (_____) | x | (_____) | x | (_____) | = | ______ |
| Gen. Support Equip. | 2.6 | x | (_____) | x | (_____) | x | (_____) | = | ______ |
| Scope Adjustments | | | | | | | | | |
| Chimney | (_____) | x | (_____) | x | (_____) | x | (_____) | = | ______ |
| Boiler | (_____) | x | (_____) | x | (_____) | x | (_____) | = | ______ |
| Draft Controls | (_____) | x | (_____) | x | (_____) | x | (_____) | = | ______ |
| Demolition & Relocation | (_____) | x | 1.0 | x | (_____) | x | (_____) | = | ______ |
| Other | (_____) | x | (_____) | x | (_____) | x | (_____) | = | ______ |

(A) Total Process Capital (Sum of Retrofit Cost) ______

(B) Escalated Total Process Capital, A x (____) = ______

(C) General Facilities (0 to 15% of B)B x (____) = ______

(D) Engineering and Home Office Fees = ______
(10 to 15% of B) 10% + (_____) + (_____)

(E) Total Plant Cost TPC, (B + C + D) = ______

(F) AFDC
1 yr = 0, 2 yr = .018, 3 yr = .037, (____, AFDC) x (____, TPC) = ______

(G) Total Plant Investment TPI, (E + F) = ______

(H) Royalty Allowance = ______

(I) Preproduction Costs (2% of G) = ______

(J) Inventory Capital = ______

(K) Initial Catalyst & Chemicals = ______

(L) Total Capital Retrofit Requirement = ______
(G + H + I + J + K)

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* Base Process Cost shown includes EPRI standard project and process contingencies. Costs shown are for a 500 MW conventional limestone FGD process.

## TABLE 2. SOIL-GEOTECHNICAL FACTORS

| DESCRIPTION | REAGENT FEED | SULFUR DIOXIDE REMOVAL | FLUE GAS | WASTE HANDLING | GEN. SUPP EQUIPMENT | CHIMNEY |
|---|---|---|---|---|---|---|
| Insitu soils are dense, having a bearing capacity of 4 ksf and over, or existing structural fill, footings can be placed after excavation. | 0.93 | 0.97 | 0.93 | 0.95 | 0.93 | 0.95 |
| Loose insitu soils, excavation & replacement with compacted structural fill is required. | | | | | | |
| A. Sandy clay | 0.96 | .98 | .96 | .97 | .96 | .97 |
| B. Sand | 0.97 | .99 | .97 | .98 | .97 | .98 |
| C. Loose sand | 0.98 | .99 | .99 | .99 | .99 | .99 |
| D. Very loose silt | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Poor bearing capacity soils with deep bedrock formation. Bearing or friction type pile is the most feasible solution. | | | | | | |
| Bedrock is: | | | | | | |
| A. 25' below surface(base case) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| B. 35' below surface | 1.01 | 1.0 | 1.01 | 1.01 | 1.01 | 1.01 |
| C. 50' below surface | 1.03 | 1.01 | 1.03 | 1.02 | 1.03 | 1.02 |
| D. 75' below surface | 1.04 | 1.01 | 1.04 | 1.03 | 1.04 | 1.03 |
| E. 100'below surface | 1.06 | 1.02 | 1.06 | 1.04 | 1.06 | 1.04 |
| F. 125'below surface | 1.07 | 1.02 | 1.07 | 1.05 | 1.07 | 1.05 |
| *Limited headroom requiring special drilling or driving equipment; add to above. | .08 | .025 | .075 | .05 | .075 | .05 |

## TABLE 2. SOIL-GEOTECHNICAL FACTORS

| DESCRIPTION | REAGENT FEED | SULFUR DIOXIDE REMOVAL | FLUE GAS | WASTE HANDLING | GEN. SUPP EQUIPMENT | CHIMNEY |
|---|---|---|---|---|---|---|
| Poor bearing capacity soils with presence of ground water, shallow bedrock, drilled piers are necessary. | | | | | | |
| A. Ground water at 10' | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| B. Ground water at 5' | 1.01 | 1.0 | 1.01 | 1.01 | 1.01 | 1.01 |
| C. Ground water at 3' | 1.03 | 1.01 | 1.03 | 1.02 | 1.03 | 1.02 |
| | 1.07 | 1.02 | 1.07 | 1.05 | 1.07 | 1.05 |
| Flood plain or by river bank, drilled piers are suitable. Caisson liner & wet drilling are necessary. | | | | | | |
| *Limited headroom requiring special drilling or driving equipment. Add to above. | .08 | .025 | .075 | .05 | .075 | .05 |

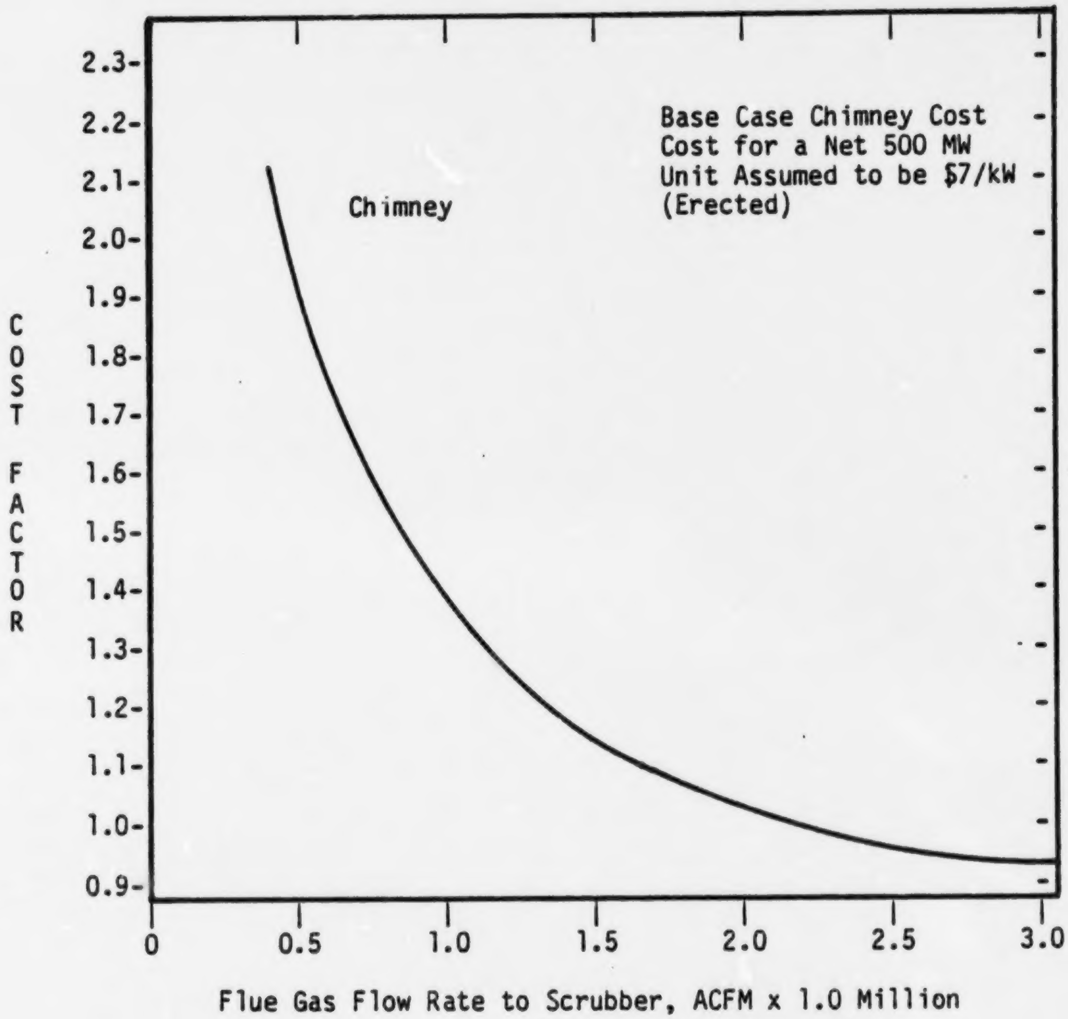

Figure 3. Process Flow Rate Scope Adjustments

## TABLE 3. FIRST-YEAR O&M COSTS SUMMATION SHEET

Fixed O&M Cost

A) Operating Labor ______ $/kW-Yr.

B) Maintenance Labor ______ $/kW-Yr.

C) Maintenance Material ______ $/kW-Yr.

D) Administrative and Support Labor ______ $/kW-Yr.

Total Fixed O&M Cost (A+B+C+D) ______ $/kW-Yr.

Variable O&M Cost

E) Reagent Consumption

1) Lime ______ $/kW-Yr.
2) Limestone ______ $/kW-Yr.

Total Reagent Consumption (1+2) ______ $/kW-Yr.

F) Steam Usage Cost ______ $/kW-Yr.

G) Power Usage Cost ______ $/kW-Yr.

H) Water Usage Cost ______ $/kW-Yr.

I) Waste Disposal Cost ______ $/kW-Yr.

Total Variable O&M Cost (E+F+G+H+I) ______ $/kW-Yr.

## CONCLUSION

The estimating guidelines presented in this study provide a consistent methodology that allows the user to estimate site specific retrofit cost. The procedure should save the user considerable time in assessing the cost of FGD options available for retrofit. FGD processes to which this procedure is directly applicable include conventional wet limestone, lime dual alkali, forced oxidation of limestone, lime spray drying, Chiyoda Thoroughbred 121, and Wellman-Lord. Simplified selection logic provided in the final report should aid the utility engineer in his selection of a process design for retrofit evaluation.

# COMPARATIVE COSTS OF
# $SO_2$ REMOVAL TECHNOLOGIES

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## ABSTRACT

### Comparative Costs of $SO_2$ Removal Technologies

The costs of retrofitting four types of in-plant $SO_2$ control technologies are compared for a 500 MW pulverized coal-fired utility boiler. Technologies examined are at various stages of commercialization and market penetration, and include: (1) fully commercial - limestone FGD, (2) early commercial - adipic acid enhanced FGD, (3) early commercial - lime spray drying, and (4) developmental - limestone injection multistage burners. Cost comparisons are made by process subarea, by operating cost categories, by capital to operating cost ratio, and by overall sulfur removal effectiveness.

# COMPARATIVE COSTS OF $SO_2$ REMOVAL TECHNOLOGIES

## I. INTRODUCTION

As a single emission source category, coal-fired utility boilers represent the largest source of $SO_2$ in the eastern United States. The options for reducing $SO_2$ emissions from this source category include alternative generating technology (e.g., nuclear and hydroelectric), fuel switching (e.g., to low sulfur coal, oil, or gas), coal cleaning, and retrofit of in-plant $SO_2$ control technology. The objective of this paper is to compare the cost and performance characteristics of four retrofittable in-plant $SO_2$ control technologies: (1) limestone flue gas desulfurization (FGD), (2) adipic acid enhanced limestone FGD, (3) lime spray drying, and (4) limestone injection multistage burners (LIMB). Note that these technologies are at various stages of commercialization or market penetration, and that they represent different degrees of $SO_2$ control in terms of percent removal. For example, conventional limestone FGD is a fully commercial process; adipic acid enhanced limestone FGD has been demonstrated on a commercial scale and is beginning to penetrate the FGD market; lime spray drying is in the early commercial phase for western U.S. coals, and in the demonstration phase for eastern U.S. coal applications; and LIMB technology is clearly in the developmental phase.

It is important to note that the cost comparisons made here are of a general nature only and cannot be used to distinguish the benefits or disadvantages of different technologies for a site-specific application. Selection of a preferred $SO_2$ control technology for any given site must be made on the basis of site-specific conditions and performance requirements (e.g., percent $SO_2$ removal required, existing ductwork arrangement, coal type, capacity). However, developing costs on a consistent basis (e.g., for retrofit on a 500 MW boiler firing 3.5 percent sulfur bituminous coal) and with a uniform cost methodology will be useful to environmental policy analysts who need general cost and performance characteristics for in-plant retrofittable $SO_2$ control technologies. This analysis is also useful in quantifying the range of potential cost benefits for emerging technologies such as LIMB, as well as the benefits of enhancements to existing conventional technology such as the adipic acid enhancement to limestone FGD.

## II. METHOD OF ANALYSIS AND DESIGN BASES

In comparing the costs of the four technologies, it was desired to illustrate clearly where differences between the technologies exist, as well as to make overall cost and performance comparisons of the four technologies. To accomplish this, the method of analysis chosen was to compare direct investment costs for various process subareas and operating expense categories. After examining direct investment or process subareas and operating expense categories, the usual parameters of total capital investment ($/kW) and net annual operating expense (mills/kWh) were accumulated for each of the four technologies. Then, using a uniform fixed charge rate (16 percent), the annual revenue requirement attributable to the control technology was computed. To examine the differences in capital intensity for the four technologies, the capital investment to operating expense ratio was computed. Lastly, a composite cost and performance parameter of $/ton* $SO_2$ removed was computed for each technology. The methods of comparing costs are summarized in Table 1.

Key design bases for this study were: retrofit to a 500 MW boiler firing 3.5 percent eastern U.S. bituminous coal. To account for retrofit, a 30 percent penalty was added to all estimates of process capital direct investment. It was assumed that the boiler would have 20 years remaining life at 5500 hr/yr subsequent to the retrofit. Although it is acknowledged that these assumptions are optimistic relative to current expectations of boiler life and capacity utilization, there is a trend in the utility industry toward extending useful plant lifetime. All costs are presented in 1983 dollars. These design assumptions are summarized in Table 2.

The cost estimates used in this study are based on previous estimates prepared for EPA by the Tennessee Valley Authority's Office of Power (1,2). The limestone FGD and limestone adipic acid FGD costs are based on estimates provided in Reference 1, and the lime spray dryer costs are based on estimates provided in Reference 2. The basis for the LIMB cost estimate is discussed below.

Note that different $SO_2$ removal efficiencies are assumed for the four technologies: limestone FGD - 90 percent, limestone adipic acid FGD - 90 percent, lime spray drying - 70 percent, and LIMB - 55 percent. Clearly, these differences must be considered when comparing the capital investments and operating expenses. However, a major objective of this analysis is to compare the cost-effectiveness of the technologies in terms of dollars per ton $SO_2$ removed. For this reason, the design basis removal efficiencies were assumed at levels characteristic of the technology capabilities and expected typical applications.

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*Short tons are used here for the convenience of the reader. This may be converted to metric units by noting 1 short ton equals 907.2 kg. See Table of Conversion Factors at end of paper.

### TABLE 1. METHODS OF COST COMPARISONS

- Process subarea direct investments
- Operating expense categories
- Total capital investment ($/kW)
- Net annual operating expense (mills/kWh)
- First year annual revenue requirement (mills/kWh)
- Capital investment to operating expense ratio
- Cost and performance ($/ton $SO_2$ removed)

### TABLE 2. GENERAL DESIGN BASES FOR FOUR TECHNOLOGIES COMPARED

- Retrofit to 500 MW
- Eastern U.S. coal-fired boiler
- 3.5% Sulfur bituminous coal
- 20 years remaining life at 5500 hr/year
- All costs presented in $1983

For the limestone FGD and limestone adipic acid FGD cases, a design employing spray tower absorbers, and utilizing forced oxidation with landfill disposal of solid waste was used (1). The design also included one spare absorber train, emergency bypass of 50 percent of the scrubbed gas, and reheat to 79.4°C (175°F). The battery limits for the capital cost estimates began with the inlet plenum downstream of the ESP and extended to (but did not include) the stack plenum. The calcium to sulfur ratio for limestone FGD was 1.4, and for adipic acid limestone FGD, 1.07. All estimates were adjusted to reflect mid-1983 dollars. A 30 percent retrofit penalty was applied to all process capital direct investment items, and for total indirect capital items, a uniform factor of 45 percent of total capital investment was assumed.

Adjustments to the TVA estimates for lime spray drying (2) on high sulfur eastern coal were more substantial than adjustments to the TVA limestone FGD cases (1). Material handling and feed preparation estimates for lime spray drying were adjusted downward to reflect a calcium to sulfur ratio assumption of 1.3 as opposed to the TVA assumption of 1.5. Note that the lime spray drying retrofit system examined here assumes retrofit to an existing 500 MW unit with an existing electrostatic precipitator. No fabric filter was included in the retrofit, in contrast to the TVA estimate for a new lime spray drying system with a fabric filter (2). However, provision for 0-10 $/kW increment to the direct investment for the lime spray dryer was made for possible upgrading of the particulate control system. This translates into an additional total capital investment cost of about 0-20 $/kW, when the indirect capital is added. Also for the lime spray drying estimates, the solid waste disposal estimates were reduced so that this cost reflected the incremental cost due to the additional solid waste from the sorbent (reacted and unreacted). The original TVA estimate appears to provide for solid waste of both coal fly ash and sorbent. Other adjustments made here are the same as for the other technologies and include the 30 percent retrofit penalty to process capital direct investment as well as adjustments for 1983 dollar basis.

Capital investment costs were compared for each process subarea noted in Table 3. Operating expense categories examined are noted in Table 4. Note that these do not include capital related charges, which are treated later as a component of first year revenue required.

In the estimation of raw material expenses, sorbent costs were estimated according to stoichiometric ratios of 1.4 for limestone FGD, 1.07 for adipic acid limestone FGD, 1.3 for lime spray drying, and 3.6 for LIMB. Stoichiometric ratio is defined here as moles Ca per mole $SO_2$ absorbed. Note that for LIMB, the calcium to sulfur stoichiometric ratio is usually expressed as moles of calcium per mole of sulfur in coal. At 55 percent sulfur capture, the stoichiometric ratio of 3.6 based on sulfur absorbed is equivalent to a stoichiometric ratio of 2 based on inlet sulfur. The cost of limestone delivered was assumed to be $15/ton, and for lime, $55/ton.

TABLE 3. PROCESS SUBAREAS COMPARED

- Materials handling and preparation
- Gas handling and $SO_2$ absorption
- Boiler and burner modifications
- Oxidation, reheat, solids thickening
- Particulate control system upgrade
- Solid waste disposal (landfill)

TABLE 4. OPERATING EXPENSE CATEGORIES

- Raw materials
- Operating labor and supervision
- Utilities
- Maintenance, labor, and materials
- Analysis
- Plant and administrative overhead

## III. RESULTS

The estimated direct investment for each subarea is detailed in Table 5. In the materials handling and preparation area, notice that the estimated direct investment costs are very similar for limestone FGD, limestone adipic acid, and lime spray drying with all of these at approximately \$20/kW. The lower direct investment for the LIMB materials handling and preparation area is primarily due to the much simpler sorbent preparation process which consists of crushing and grinding. One reason for the lower LIMB limestone preparation equipment is that the other systems examined require make-down, storage, and pumping of sorbent slurries. The materials handling direct investment used for LIMB was estimated to be the same as for limestone FGD. The estimate of the sorbent preparation (i.e., crushing and grinding) for LIMB, was obtained by scaling-up an estimate for LIMB limestone preparation on a 200 MW system (3).

From Table 5, it is also seen that the gas handling and $SO_2$ absorption areas are the single largest components of the capital investment for the first three processes. For purposes of comparison, the analagous LIMB process area can be thought of as the boiler and burner modifications required to achieve $SO_2$ capture. This LIMB item was estimated on the basis of low-$NO_x$ B&W dual-register burners with lighters equipped for limestone injection, modification to boiler pressure parts, new control system, and new coal and limestone feeder (3). Due to the uncertainty and site-specific variability expected for this item, a range of 5-15 \$/kW has been given. Retrofit of a dual register or distributed mixing burner to an existing wall-fired boiler that does not have outboard or tertiary air ports would indeed require modification to pressure parts for retrofit installation. However, if an internally staged low-$NO_x$ burner were employed, the retrofit would not require the costly modification to the boiler tubes proximate to the burner.

Miscellaneous process areas contributing to the capital costs of limestone FGD and limestone adipic acid FGD include oxidation, reheat, and solids thickening. That these process areas are not applicable to either lime spray drying or LIMB explains some of the cost benefits of spray drying and LIMB relative to wet FGD. The contribution of oxidation, reheat, and solids thickening to direct investment is given in Table 5.

For both the lime spray drying and LIMB technology, we assume that 0-10 \$/kW in direct investment will be required for potential particulate control system upgrade. This is to cover, if needed, gas conditioning (e.g., humidification, $SO_3$ conditioning), increased ESP plate area for higher grain loadings, and upgraded solids handling equipment.

In this analysis, solid waste disposal costs are treated by assigning direct investment estimates to landfill construction and landfill equipment. This, of course, has the effect of increasing the estimate of capital relative to the case where estimates of solid waste disposal costs are handled strictly as an operating expense. This item adds

TABLE 5. ESTIMATES OF DIRECT INVESTMENT FOR DIFFERENT PROCESS SUBAREAS

| | Estimated Direct Investment, \$/kW[a,b] | | | |
|---|---|---|---|---|
| | Limestone | Limestone Adipic Acid | Lime Spray Drying | LIMB |
| Materials handling and preparation | 20.4 | 19.2 | 19.2 | 8.9 |
| Gas handling and $SO_2$ absorption | 88.6 | 79.1 | 57.4 | |
| Boiler and burner modifications | | | | 5-15 |
| Oxidation, reheat, solids thickening | 28.0 | 25.3 | | |
| Particulate control system upgrade | | | 0-10 | 0-10 |
| Solid waste disposal (landfill) | 10.0 | 8.7 | 8.5 | 9.2 |
| Total direct investment | 147.0 | 132.3 | 85.1-95.1 | 23.1-43.1 |

[a] All cost estimates for direct investment were adjusted to 1983\$ using Marshall and Stevens installed equipment cost indices, assuming a 1983 M&S equipment index of 759.

[b] Direct investment estimates include a 6 percent add-on for services and utilities, and a 30 percent retrofit penalty for all process subareas except solid waste.

approximately $10/kW of direct investment (about $20/kW total capital) to each retrofit control technology. The variation noted in Table 5 is ascribed to differences in the quantity and characteristics of solid waste generated by the four processes.

Indirect capital was estimated at 45 percent of total capital investment for all technologies examined. This includes indirect fixed investment (e.g., engineering design and supervision, architect and engineering contractor, construction expense, contractor fees, and contingencies), and non-depreciable capital investment items (e.g., allowance for start-up and modifications, interest during construction, royalties, land, and working capital). Although this fraction of total capital for indirect investment is somewhat greater than usually recommended for either solid processing or solid/fluid processing, it is consistent with the ratio used in the more detailed estimates provided in References 1 and 2. The contingency component of indirect investment would normally be increased for a developmental process such as LIMB. This adjustment is not made here since generous contingencies for the developmental process subareas have already been accounted for in the expressed range of direct investment for boiler and burner modification, and upgrade to particulate matter control. Direct investment, indirect capital costs, and total capital investment are summarized in Table 6.

Operating expense categories examined for the four technologies are listed in Table 4, and the results for operating expenses are summarized in Table 7. In the case of raw materials, the higher cost for lime spray drying relative to the other three technologies clearly reflects the higher cost per ton of lime ($55/ton) versus limestone ($15/ton). For the three technologies employing limestone sorbent, the raw materials cost estimates in general are proportional to the calcium to sulfur ratio with a slight exception for the limestone adipic acid case which includes the incremental costs of the adipic acid. The lower operating labor and supervision costs, also noted in Table 7, for lime spray drying and LIMB relative to limestone and limestone adipic acid reflect the simpler nature of the former two processes.

The operating expense category of utilities includes direct operating costs for steam, process water, electricity, and diesel fuel. Electricity consumption represents the major cost element in this category and is due primarily to providing motive power for crushing and grinding, materials handling, and pumping. The estimates for electricity and other utilities are also presented in Table 7. Note that the electricity consumption is greatest for the limestone process and least for lime spray drying. Although one might expect the electricity assumption for LIMB to be similar to that for the lime spray drying system, a higher value was used to reflect the increased requirement for grinding and crushing due to the larger amount of sorbent. Steam requirements for limestone adipic acid are about 20 percent less than for conventional limestone due primarily to lower reheat requirements. No steam requirements were assumed for either lime spray drying or LIMB. However, an energy penalty for calcination of limestone was introduced into this category for the LIMB process.

TABLE 6. TOTAL CAPITAL INVESTMENT SUMMARY

| | Direct Investment $/kW | Indirect Capital Costs[a] $/kW | Total Capital Investments $/kW |
|---|---|---|---|
| Limestone | 147 | 120 | 267 |
| Limestone adipic acid | 132 | 108 | 240 |
| Lime spray drying | 85-95 | 70-78 | 155-173 |
| LIMB | 23-43 | 19-35 | 42-78 |

[a] Indirect capital estimated at 45% of total capital investment.

## TABLE 7. ANNUAL OPERATING EXPENSES BY CATEGORIES

| | Annual Operating Expense, mills/kWh | | | |
|---|---|---|---|---|
| | Limestone | Limestone Adipic Acid | Lime Spray Drying | LIMB |
| Raw materials[a] | 0.78 | 0.67 | 1.95 | 1.23 |
| Operating labor and supervision | 0.44 | 0.40 | 0.29 | 0.23 |
| Utilities | | | | |
| Steam[b] | 0.46 | 0.36 | -- | 0.28 |
| Water | 0.01 | 0.01 | 0.01 | -- |
| Electricity | 0.73 | 0.57 | 0.47 | 0.62 |
| Diesel Fuel | 0.05 | 0.03 | 0.01 | 0.02 |
| Maintenance, labor, and materials[c] | 2.05 | 1.84 | 1.36 | 0.53 |
| Analysis | 0.04 | 0.02 | 0.03 | 0.03 |
| Plant and administrative overhead[d] | 1.52 | 1.36 | 1.01 | 0.47 |
| Net annual operating expenses | 6.08 | 5.26 | 5.13 | 3.41 |

[a] Limestone and lime costs were assumed at $15/ton and $55/ton, respectively, on a delivered basis.

[b] Steam for limestone and limestone adipic acid was for reheat; although no steam was required for LIMB process, a calcination energy penalty of 1400 kJ/kg (600 Btu/lb) limestone was added here.

[c] Maintenance, labor, and materials were estimated at 8 percent of direct process investment plus 3 percent of waste disposal investment.

[d] Plant and administrative overhead was estimated at 60 percent of the sum of operating labor, maintenance, and analysis.

For this purpose it was assumed that 600 Btu/lb* limestone was required for calcination. Process water costs are a minor component of utilities and contribute on the order of 1 percent to the utility cost category. Diesel fuel expenses relate primarily to the solid waste disposal area, and in general vary with the amount of solid waste generated per process.

Maintenance, labor, and materials represent an important component of the net annual operating expenses as indicated in Table 7. As in the EPA/TVA studies (1,2) these expenses were estimated at 8 percent of direct process investment plus 3 percent of the waste disposal investment. Again, the higher maintenance labor and materials expenses for limestone and limestone adipic acid reflect the more complex nature and more capital equipment intensive feature of these processes relative to lime spray drying and LIMB.

Plant and administrative overhead expenses are indirect operating expenses. They are estimated at 60 percent of process conversion expenses minus utilities expense. This is equivalent to 60 percent of the sum of operating labor and supervision; maintenance, labor, and materials; and laboratory analysis. Plant and administrative overhead expenses are noted in Table 7.

Net annual operating expenses are defined as the sum of the annual direct operating expenses plus the indirect plant and administrative overhead. Note that net annual operating expenses is analogous to the frequently used term "total operating and maintenance (O&M)" expense, and does not include capital related charges. The net annual operating expenses for the four processes examined are given at the bottom of Table 7. Note that the net annual operating expenses for LIMB are substantially lower than for the other three processes. It is expected that the lime spray drying net annual operating expenses would be more comparable to LIMB except for the high cost per ton of lime relative to limestone.

Revenue requirement estimates are presented as first year annual revenue requirements. For each process the revenue requirement is equal to the sum of the capital charge and the net annual operating expense. The capital charge is computed by multiplying a fixed charge rate of 16 percent times the total capital investment. The 16 percent fixed charge rate results from the economic assumptions noted in Table 8. It is expected that shortening the anticipated remaining life of the process from 20 to 15 or 10 years would have a substantial impact on the fixed charge rate, resulting in higher annual capital charges. Table 9 details the capital charges, operating expenses, and revenue requirements for the four processes.

A measure of the capital intensity of each process is taken as the ratio of the annual capital charge to the net annual operating expense. These ratios are listed in Table 10, and indicate the varying degrees of capital intensity for the four processes examined. The most notable difference is the low capital intensity feature of the LIMB process relative to

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*To convert to metric, see Table of Conversion Factors at end.

## TABLE 8. ECONOMIC PREMISES FOR FIXED CHARGE RATE

| | |
|---|---|
| System lifetime | 20 years |
| Accounting lifetime | 10 years |
| Method of depreciation | straight line |
| Income tax rate | 50 percent |
| Investment tax credit | 10 percent |
| Property tax and insurance | 2.25 percent |
| Weighted cost of capital, after tax | 10 percent |
| Fixed charge rate (resulting from above) | 16 percent |

## TABLE 9. FIRST YEAR ANNUAL REVENUE REQUIREMENT

| | Capital Charge mills/kWh | Net Annual Operating Expense mills/kWh | First Year Annual Revenue Requirement mills/kWh |
|---|---|---|---|
| Limestone | 7.8 | 6.1 | 13.9 |
| Limestone adipic acid | 7.0 | 5.3 | 12.3 |
| Lime spray drying | 4.5-5.0 | 5.1 | 9.6-10.1 |
| LIMB | 1.2-2.3 | 3.4 | 4.6-5.7 |

## TABLE 10. CAPITAL TO OPERATING EXPENSE RATIO[a]

| | |
|---|---|
| Limestone | 1.3 |
| Limestone adipic acid | 1.3 |
| Lime spray drying | 0.9 |
| LIMB | 0.5 |

[a] Ratio presented here is defined as the annual capital charge divided by the net annual operating expense.

## TABLE 11. COST AND PERFORMANCE SUMMARY

| | Revenue Requirement mills/kWh | $SO_2$ Removal Efficiency % | Cost Effectiveness \$/ton $SO_2$ Removed |
|---|---|---|---|
| Limestone | 13.9 | 90 | 620 |
| Limestone adipic acid | 12.3 | 90 | 550 |
| Lime spray drying | 9.6-10.1 | 70 | 550-580 |
| LIMB | 4.5-5.6 | 55 | 330-410 |

limestone and limestone adipic acid, with lime spray drying having an intermediate capital intensity ratio. The low capital intensity feature of LIMB will tend to improve its already favorable cost-effectiveness relative to more capital intensive processes, for shorter lifetime, lower capacity applications. For this reason, the economic preference for LIMB in a retrofit application should be even stronger than that shown here.

## IV. SUMMARY

In summary, the costs of limestone and limestone adipic acid FGD are substantially higher than those for either lime spray drying or LIMB, although the former two processes achieve a 90 percent $SO_2$ removal efficiency while lime spray drying and LIMB achieve 70 and 55 percent $SO_2$ removal, respectively. The lime spray drying process estimated here was assumed to achieve an $SO_2$ removal efficiency of 70 percent, and the LIMB process, an $SO_2$ removal efficiency of 55 percent. To compare the cost per unit of $SO_2$ removed, the \$/ton of $SO_2$ removed was computed for each of the four processes. These results are listed in Table 11. Note that the effectiveness of lime spray drying retrofit to an eastern U.S. high-sulfur coal-fired boiler is very similar to limestone adipic acid FGD, certainly within the range of uncertainties in these estimates. Both the limestone adipic acid and lime spray drying appear to be slightly more cost-effective than conventional limestone FGD. Even within the range of uncertainty in the LIMB cost estimate, the cost-effectiveness parameter for LIMB is 50 to 90 percent more favorable than the cost-effectiveness parameter for conventional limestone FGD. This economic preference, coupled with the simplicity of the LIMB process relative to conventional FGD, suggests that LIMB has a strong potential for medium performance applications on retrofit $SO_2$ control technology for eastern U.S. high-sulfur coal-fired boilers.

## V. TABLE OF CONVERSION FACTORS

| Multiply | By | To Obtain |
|---|---|---|
| ton (short) | 907.2 | kg |
| \$/ton | $1.102 \times 10^{-3}$ | \$/kg |
| Btu/lb | 2.326 | kJ/kg |

## VI. REFERENCES

1. Burnett, T.A., et al. (Tennessee Valley Authority). Economic Evaluation of Limestone and Lime Flue Gas Desulfurization Processes, EPA-600/7-83-029 (NTIS PB84-133644), May 1983.

2. Burnett, T.A., and K.D. Anderson (Tennessee Valley Authority). Technical Review of Dry FGD Systems and Economic Evaluation of Spray Dryer FGD Systems, EPA-600/7-81-014 (NTIS PB81-206476), February 1981.

3. Private communication with R. Johnson, Tennessee Valley Authority, September 1983.

## SESSION 3: MATERIALS OF CONSTRUCTION

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# EPRI RESEARCH ON CORROSION AND DEGRADATION OF MATERIALS FOR FGD SYSTEMS

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## ABSTRACT

An EPRI survey of materials problems in full-scale lime/limestone wet scrubbers in the USA revealed that the most frequent and most critical failures occurred in the outlet ducts and the stack, but that a significant number of failures also occurred in the prescrubbers, absorbers, reheaters, dampers, pumps, piping and valves. The root cause of most of these failures was corrosion or degradation of the materials of construction. Over the last few years, EPRI has initiated a multitude of projects aimed at understanding and eliminating corrosion induced failures in scrubbers. Primary emphasis has been on metallic materials, but an increasing amount of effort is being directed towards coatings, nonmetallic materials of construction, and corrosion control techniques. The range of EPRI's research on corrosion and degradation of materials for FGD systems is described in this paper.

## BACKGROUND

Some of the more critical corrosion problems faced by the U.S. utility industry are in the flue gas path between the coal-fired boiler and the top of the stack. High-sulfur and medium-sulfur coals are being used to an increasing extent and, with the introduction of ever more stringent environmental control laws, utilities have been required to remove a large percentage of the sulfur dioxide ($SO_2$) from the flue gas before it is emitted from the stack. Among the flue gas desulfurization (FGD) systems that have been devised, lime and limestone scrubbers are the most developed. Typically, flue gas at about 150°C (300°F) will enter the quench section of a scrubber (the "prescrubber") then flow through a spray of lime or limestone slurry delivered from nozzles at the top of the scrubber. As the gas passes through this spray zone (the "absorber"), $SO_2$ and other acid gases are absorbed and neutralized by the slurry. The scrubbed gas leaves the absorber at the adiabatic saturation temperature, typically 50-55°C (120-130°F); it then passes through mist eliminators and on to the stack. Unless some type of reheat system is installed after the mist eliminators, the water-saturated gas condenses on the walls of the duct leading to the stack and on the stack lining. These condensates can be very corrosive. Reheaters are sometimes used to raise the temperature of the outlet gas to 70-95°C (160-200°F) so that corrosion in the outlet duct and stack is minimized and so that the gas is more buoyant and the plume is less visible.

A survey of all full-scale lime/limestone wet scrubbers in the U.S.A. was performed for EPRI in 1980 to establish the type and frequency of materials related problems being experienced in FGD systems (1). The survey revealed that all manner of construction materials have been used, including metals, organic coatings and linings, and ceramic and other inorganic materials. The most frequently cited problem areas were the outlet ducts and the stack, both of which are particularly critical components in that failures may require boiler shutdown and loss of generating capacity. Less frequent and less critical failures were noted in the prescrubbers, absorbers, reheaters, dampers, pumps, piping, and valves. This survey made it clear that corrosion and, to a lesser extent, erosion were causing extensive and very costly problems in power plant FGD systems. There appeared to be no consensus on the choice of construction materials, and this uncertainty was not improved by reports that materials that worked well in one scrubber failed miserably in another. As a consequence, EPRI initiated a number of projects to identify materials degradation problems in FGD systems and to develop solutions to those problems.

## MATERIALS RELATED RESEARCH

Table 1 lists by research project (RP) number the past and present EPRI contracts related to corrosion and degradation of materials in FGD environments. Also listed are the relevant periods of performance, project titles, contractor's names, and resulting EPRI reports. Completion dates are missing for those projects still in progress.

In this paper, the objectives of each of the projects listed in Table 1 are summarized and a few of the more interesting results are discussed. Also included is the history of the development of simulated scrubber environments for laboratory testing purposes.

## OBJECTIVES OF RESEARCH PROJECTS

### RP982-14: Construction Materials for Wet Scrubbers

As mentioned above, one of the objectives of this project was to collect and summarize data on materials of construction used in full-scale utility lime and limestone FGD systems. This was achieved by visiting all existing lime and limestone sites, most of the FGD system vendors, and several coating suppliers. The data collected were quite difficult to interpret: materials that had enjoyed success in one scrubber had failed in another and, because maintenance records were sparse or absent, the cause of the failures could seldom be determined. One of the most controversial subjects was the cause of coating failures. The suppliers typically blamed faulty application (too humid, rust bloom, unsuitable surface profile, too cold etc.) whereas, the users were left wondering whether the coating itself had had inadequate chemical resistance to the harsh environments inside the FGD system.

TABLE 1. EPRI RESEARCH PROJECTS ON CORROSION AND DEGRADATION OF MATERIALS IN FGD ENVIRONMENTS

| Project No. | Period of Performance | Project Title and Contractor | EPRI Reports |
|---|---|---|---|
| RP982-14 | 10/78-2/81 | Construction Materials for Wet Scrubbers. (Battelle Columbus Labs.) | CS1736 (Vols. 1 & 2) |
| RP982-19 | 2/80-11/80 | Screening Study for Corrosion Inhibitors in $SO_2$ Removal Systems (SumX Corporation) | |
| RP1871-1 | 6/80-6/81 | Corrosion-Resistant Alloys for Flue Gas Desulfurization Systems (Battelle Columbus Labs.) | CS2533<br>CS2537 |
| RP1871-2 | 3/81- | Corrosion/Erosion Laboratory and Field Testing (Battelle Columbus Labs.) | (Report pending) |
| RP1871-3 | 5/81- | Construction Material for Wet Scrubbers Update (Battelle Columbus Labs.) | (Report pending) |
| RP1871-4 | 10/81-12/82 | Corrosion Field Testing Support Effort at R. D. Morrow (Burns and McDonnell) | CS3240 |
| RP1652-2 | 11/81- | Cyclic Reheat Materials Evaluation (Stearns Roger/Battelle Columbus Labs.) | |
| RP2248-2 | 10/82- | Materials Failure Causes in FGD Systems I (Radian Corp./Stearns Roger) | |
| RP1871-5 | 10/82- | Mechanisms of Failure of Coating Used in FGD Systems (Lehigh University) | |
| RP1871-6 | 11/82- | Corrosion Chemistry of $SO_2$ Scrubbers (Battelle Columbus Labs.) | |
| RP2248-3 | 12/82- | Materials Failure Causes in FGD Systems II (Battelle Columbus Labs./ Black and Veatch) | |
| RP1871-7 | 2/83- | Effect of $SO_2$ Scrubber Chemistry on Corrosion (Rockwell International) | |
| RP1871-11 | | Characterization of Ceramic Materials for Electric Power Plant Applications (Ohio State University) | |
| RP1871-10 | | Corrosion Inhibitors for FGD Systems (Contractor not yet selected) | |

## RP1871-3: Construction Materials for Wet Scrubbers Update

As the project title suggests, this is an update of the RP982-14 survey. Now almost complete, the project included visits to all the lime and limestone wet scrubbers visited in the course of RP982-14 and a reevaluation of the materials of construction data. This information was supplemented with data on materials used in the construction of all new lime and limestone scrubbers not included in the initial survey and with data on materials used in other types of FGD systems, including spray dryers, dual alkali systems, Wellman-Lord systems, and non-recovery $Na_2CO_3$ wet scrubbers. It is anticipated that the results of this work will be published in an EPRI report before the end of 1983.

## RP1871-1: Corrosion-Resistant Alloys For FGD Systems

This project was one of the first aimed at improving our understanding of the nature of corrosion and degradation of materials in $SO_2$ scrubbers. A literature review was performed in which field data were combined with releant laboratory test data to create a state of the art report on corrosion of alloys and linings in FGD systems (2). Recognizing that outlet ducts were particularly prone to failure, it was decided that candidate alloys and linings would be evaluated in the laboratory in simulated duct environments to determine their resistance to the various forms of corrosion and degradation. Two simulated duct environments were employed: both were acid mists generated in a fog cabinet at 48°C by atomizing solutions containing sulfurous acid and calcium chloride. In one case, the pH was adjusted to 1.0 with hydrochloric acid while, in the other case, the pH was adjusted to the same value with sulfuric acid (Table 2). Thus, the first mist contained only 200 $g/m^3$ * chloride (from the calcium chloride) whereas the second mist contained 5000 $g/m^3$ chloride (from both the calcium chloride and the hydrochloric acid). To simulate exposure to the hot dry flue gas under bypass conditions, some specimens were taken from the fog cabinet 5 times per week and placed in a dry oven at 120°C for 5 hours before being returned to the fog cabinet. The oxygen concentration in both the dry oven and the fog cabinet was maintained at 8% by volume, a value typically found in scrubber ducts. At

TABLE 2. SIMULATED DUCT ENVIRONMENTS AT TWO CHLORIDE LEVELS

| 200 $g/m^3$ $Cl^-$ | 5000 $g/m^3$ $Cl^-$ |
|---|---|
| 17 ml/l of 7.4% $H_2SO_3$ | 17 ml/l of 7.4% $H_2SO_3$ |
| 0.3 g/l $CaCl_2$ | 0.3 g/l $CaCl_2$ |
| 3.7 ml/l of 95% $H_2SO_4$ | 11 ml/l of 37% HCl |

---

* Concentrations quoted in $g/m^3$ are numerically equal to concentrations in parts per million by weight (ppm).

the time this work was performed (1980-81), the test environment was considered to simulate closely the environment actually found in a scrubber duct: proper consideration had been given to the form of the environment (a calcium-based condensate), the temperature (cycling between 48°C and 120°C), the pH (~1), and the chloride level (200-5000 $g/m^3$).

The results of this work (3, 4) contained no surprises: in the low-chloride environment, all alloys tested were resistant to uniform corrosion and localized attack whereas, at the higher chloride level, several of the stainless steels tested suffered a considerable amount of pitting, crevice corrosion, uniform corrosion and, in some instances, intergranular attack. The nickel alloys and titanium tested, on the other hand, appeared to be resistant to these forms of corrosion. Most of the linings tested were chemically resistant to both the low- and high-chloride acidic mists but none could withstand the temperature cycling between 48°C and 120°C: the coatings either deteriorated at the higher temperature or delaminated from the C-steel substrate.

## RP1871-2: Corrosion/Erosion Laboratory and Field Testing.

This project has been in progress for over 2 years and consists of both laboratory and field testing of a wide variety of materials of construction, including alloys and linings. The primary objective of this project is to obtain sufficient field and laboratory test data so that our understanding of the mechanisms of corrosion and degradation is greatly improved. It is hoped that, with this improved understanding, cost-effective materials of construction can be selected with much greater confidence than is currently possible.

Field tests are currently being performed at three stations burning medium-, low-, and high-sulfur coals: these are, respectively, the R. D. Morrow, Sr. Station of the South Mississippi Electric Power Association, the Clay Boswell Station of Minnesota Power Company, and Duck Creek Station of Central Illinois Light Company. Although the field test environments cannot be controlled with the precision possible in a laboratory test, a substantial effort is going into their characterization (see later, RP1871-4); and one of the tasks in RP1871-2 has been to install special condensate collectors in the outlet duct of two of the host scrubbers so that samples of the corrosive condensates can be collected for pH measurement and chemical analysis. It is hoped that the field test conditions will be sufficiently well characterized that results can be correlated with the results of the concurrent laboratory tests. However, such correlations are only possible if the corrosion processes are well understood and all relevant variables have been given proper consideration.

By the time the earlier project, RP1871-1, was drawing to a close, there was a growing concern that the aggressiveness of scrubber environments was not simply controlled by pH, temperature, and chloride content. It was recognized that scrubber environments were chemically quite complex and that some of the species present in trace or minor amounts could play a critical role in the corrosion and degradation of materials.

Thus, when the RP1871-2 laboratory studies were initiated an effort was made to more closely simulate the scrubber environments of interest, namely those found in prescrubbers, absorbers, outlet ducts, and reheaters (see Table 3).

TABLE 3. RANGE OF ENVIRONMENTAL CONDITIONS OCCURRING IN PRESCRUBBERS, ABSORBERS, OULET DUCTS, AND REHEATERS

| Component | pH range | $Cl^-$ range* $kg/m^3$ | Temp. range °F(°C) |
|---|---|---|---|
| Prescrubber | 1-4 | 5-50 | 120-300 (50-150) |
| Absorber (after prescrubber) | 4.5-7.5 | 1-5 | 120-130 (50-55) |
| Absorber (no prescrubber) | 4.5-7.5 | 1-20 | 120-300 (50-150) |
| Outlet duct | 1-4 | 1-20 | 120-130 (50-55) |
| Reheater tubes | 1-4 | 1-20 | 250-400 (120-205) |

*1 $kg/m^3$ = 1000 parts per million by weight. Chloride levels up to 100 $kg/m^3$ predicted for future closed loop scrubber systems.

Calcium-based solutions have been used throughout this progra- and the chloride levels, pH values, and temperatures have been chosen to fall within the ranges identified in Table 3. The major difference between these environments and those used in RP1871-1 is that three other species known to be present in scrubber liquids (fluoride, sodium, and magnesium ions) have been added to each simulated scrubber environment. After examining the available chemical analyses of absorber liquids, prescrubber liquids, and typical coals, the decision was made (a) to add chloride partly as $CaCl_2$ and partly as $MgCl_2$ so that a Ca:Mg ratio of 2:1 is achieved (b) to add enough fluoride to give a Cl:F ratio of 10:1, achieved primarily by adding $CaF_2$, but also by adding sufficient NaF to give a background Na content of 500 $g/m^3$. It should be noted that, quite often, not all of the $CaF_2$ addition dissolves in the test solution so that the Cl:F ratio in solution can be higher than 10:1 (4). The pH of each solution is adjusted to the desired value by adding sulfuric acid and, as in the RP1871-1 tests, the solutions are maintained in equilibrium with a nitrogen/8% oxygen gas mixture.

The fog cabinet, used previously for the simulated duct tests, is also being used at the same temperature (48°C) for the simulated reheater tests. However, the cabinet internals have been modified to allow the specimens to be locally heated to a typical reheater temperature (121°C). Prescrubber and absorber conditions are simulated in large tanks filled with the test solutions described above; specimens are immersed in the liquid and also suspended in the vapor phase above the liquid.

Some of the preliminary results of RP1871-2 were quite surprising (see Table-4).

For instance, in one series of tests in which prescrubber conditions were being simulated, the corrosion rate of all alloys increased steadily as the chloride level of a pH 1 solution was increased to 30 kg/m$^3$ (fluoride addition increased correspondingly to 3 kg/m$^3$); however, at higher halide concentrations, the corrosion rate decreased sharply (Table 4). For instance, Hastelloy Alloy C-276 had an average corrosion rate of 104 μm/y in the solution containing 30 kg/m$^3$ chloride, whereas in the 100 kg/m$^3$ chloride solution, the corrosion rate dropped to 1.4 μm/y. Even more surprizing was the observation that samples of titanium, a very corrosion resistant alloy in a wide variety of aggressive environments, disintegrated within a week in the 30 kg/m$^3$ chloride solution. Such high corrosion rates were not seen when halide concentrations were somewhat higher (Table 4) or lower; and other work (6) demonstrated that corrosion of titanium was much reduced in the absence of fluoride. Although these experiments demonstrate that fluoride can greatly accelerate corrosion in these laboratory test environments, their importance in scrubber environments has been challenged by some workers (6) who found that titanium is not susceptible to accelerated attack in similar low-pH halide solutions if flyash is also present. These workers suggest that some water-soluble ingredient in the flyash (perhaps iron or silica) is responsible for inhibiting corrosion. This observation is of great practical significance because flyash is usually carried into the scrubber with the flue gas.

TABLE 4. AVERAGE CORROSION RATES (μm/y) DURING A SIX-WEEK EXPOSURE TO SIMULATED PRESCRUBBER ENVIRONMENTS AT 93°C.

| | 30 kg/m$^3$ chloride | 100 kg/m$^3$ chloride | |
|---|---|---|---|
| Alloy | pH 1 | pH 1 | pH 4 |
| Hastelloy C-276 | 104 | 1.4 | 0.8 |
| Inconel 625 | 529 | 19.8 | 0.4 |
| 317 LM stainless | 3205 | 27.1 | 5.1 |
| 316L stainless | 4206 | 138 | 3.6 |
| Ferralium 255 | 685 | 18.3 | 1.2 |
| Titanium | >>25,000* | 8.4 | 0 |
| TiCode 12 | 1409 | 11.3 | 2.0 |

*Specimen completely dissolved in 1 week.

Results like these prompted EPRI to initiate two additional projects to investigate much more thoroughly the effects and interactions of many of the other trace elements in scrubbers (see later, RP1871-6 and RP1871-7).

## RP1871-4: Corrosion Field Testing Support Effort at R. D. Morrow

This project supports, and is closely coordinated with the field tests of RP1871-2 at the R. D. Morrow, Sr. Station of South Mississippi Electric Power Association. This plant has two 230 MW coal-fired boilers each equipped with a wet limestone scrubber representing the state of the art in closed loop, limestone FGD design. The objectives of this project are (a) to document the environment to which the RP1871-2 alloys and coatings are exposed and (b) to assist in identifying operating conditions and chemical species that lead to particularly aggressive environmental conditions. Samples of the coal, make-up water, absorber recycle slurry, demister wash water, flyash and limestone are being analyzed for trace metals, chlorides, fluorides, bromides, etc. The aggressiveness of the flue gas itself is being assessed by taking controlled condensation samples for chemical analysis and pH measurement.

## RP1871-6: Corrosion Chemistry of $SO_2$ Scrubbers.

As indicated above, this project is one of two designed to investigate more thoroughly the effects of trace and minor environmental constituents on the corrosion of alloys. Work has been underway for only a few months, but a review of the literature and all other currently available data has been completed. It was concluded that all the species listed in Table 5 may be present in FGD system environments and that their presence could affect the corrosion rates of nickel-, iron-, or titanium-based alloys.

TABLE 5. MAXIMUM CONCENTRATION OF ELEMENTS
USED IN RP1871-6 LABORATORY TEST SOLUTIONS

| Species | Max. Concn. $g/m^3$ | Species | Max. Concn. $g/m^3$ |
|---|---|---|---|
| $Mg^{2+}$ | 5000 | $NO_3^-$ | 200 |
| $Ca^{2+}$ | 1000 | $MoO_4^{2-}$ | 333 |
| $Al^{3+}$ | 2000 | | (i.e. 200 Mo) |
| $Si^{4+}$ | 100 | $PO_4^{3-}$ | 1533 |
| $Cu^{2+}$ | 1000 | | (i.e. 500 P) |
| $Cr^{3+}$ | 500 | $Cl^-$ | 100,000 |
| $Fe^{3+}$ | 2000 | $F^-$ | 10,000 |
| $Na^+$ | See note* | $Br^-$ | 500 |
| | | $I^-$ | 100 |

* $Na^+$ to be added as necessary for ionic charge balance.

Table 5 also lists the maximum concentrations considered likely in FGD system environments. These species will be investigated in the RP1871-6 laboratory test program at levels up to the quoted maxima.

Table 5 represents the distillation of information from several sources. First the chemical analyses of coals, limes, limestones, bottom ash, and flyash were reviewed. Second, the concentration of trace and minor elements in the flue gases at the inlets and outlets of two scrubbers were evaluated along with the chemical analyses of the corresponding liquid streams. Third, the concentration of elements in the condensate at the wall of the outlet ducts of two stations (collected and analyzed in RP1871-2) was assessed. Finally, available literature was reviewed to determine which of the many species present could conceivably have an effect on alloy corrosion. In addition to the dissolved solids listed in Table 5, the test solutions will contain dissolved gases, introduced by sparging the solutions with an argon carrier gas containing one or more of the following gases: $O_2$ (8% max.), $SO_2$ (0.3% max.), and $H_2S$ (5ppm by volume max.).

The great variety of species considered in the test matrix represents a formidable task, but with the help of a carefully planned statistical experimental approach, it is hoped that the effects of these species, both direct and synergistic, will be identified. Hopefully, such information will allow correlations between laboratory and field test data to be made with much greater confidence than is currently possible.

## RP1871-7: Effect of $SO_2$ Scrubber Chemistry on Corrosion

The objectives of this project are almost identical to those of RP1871-6. Indeed, the environments evaluated will be very similar, and they will also be based on the list of species shown in Table 5. However, the unique feature of this project is that primary emphasis will be on vapor phase corrosion whereas bulk liquid phase corrosion is emphasized in RP1871-6. There is evidence that the corrosion that occurs in thin condensate films is more severe than would occur in a bulk liquid of the same composition. Like RP1871-6, this project has been underway for only a few months.

## RP1871-5: Mechanisms of Failure of Coatings Used in FGD Systems

In an attempt to assess the relative importance of chemical resistance and application technique on the failure of coatings in FGD systems, RP1871-5 was initiated a little less than a year ago. The mechanisms of coating failure are being investigated in the laboratory in simulated scrubber environments. About a dozen types of coating will be evaluated ranging from vinyl esters to fluorocarbons and epoxies.

Perhaps the most critical variable being studied is surface preparation technique. Early results indicate that the adhesive strength of the coating is strongly dependent on the preparation technique used. For instance, the adherence of one fluoroelastomer to a C-steel substrate was initally much higher after chemically etching in a $HF/HNO_3$ solution than after abrading with 600-grit silicon carbide paper which, in turn, provided slightly better adherence than after a commercial alkaline washing treatment. However, after about 5 days in an acidic environment, the ranking of the surface preparation techniques was competely reversed, with the acid etch giving the poorest adherence and the alkaline wash the best.

It is hoped that this research will provide the electric utilities with the information needed to properly specify the coating application methods.

## RP1652-2: Cyclic Reheat Materials Evaluation

When the scrubbed flue gas enters the outlet duct, it is at the adiabatic saturation temperature and, in the absence of any reheat, it condenses on the walls of the duct and the stack. This condensate can be very corrosive and it has caused numerous corrosion failures in the past (see RP1871-1 and RP1871-3). Furthermore, the wet gas is not very buoyant and produces a visible plume. To circumvent these problems, some type of flue gas reheat system is often employed. Most systems are expensive to operate in that they require some external energy source to provide the heat. However, one type of reheat system, called cyclic reheat, derives the necessary heat from the hot flue gas upstream of the scrubber, so operating costs are potentially low. The cyclic reheat system most developed in the USA makes use of two in-line tube-type heat exchangers: one in the ductwork upstream of the scrubber and one in the outlet duct. Water or some other appropriate working fluid is circulated from one heat exhanger to the other so that heat, extracted from the hot (~150°C) flue gas entering the scrubber, is released to the cooler (~55°C) wet flue gas leaving the scrubber. While the concept of using "free" heat is appealing, its success depends to a large extent on the resistance of the upstream heat exchanger to corrosion and fouling. The tube wall temperature of this heat exchanger must be below that of the surrounding unscrubbed flue gas if heat is to be extracted; and, if this tube wall temperature is below the acid dew point, the resulting condensate may stimulate corrosion and encourage fouling.

EPRI initiated RP1652-2 to evaluate tube materials for the inlet gas heat extractor of a cyclic reheat system. In this work, a model heat exchanger has been designed, fabricated, and installed in a test loop at the Scholz Electric Generating Plant of Gulf Power Company. Over 20 materials are being evaluated, including some coatings. Test variables of interest are tube wall temperature and the type and frequency of tube cleaning. Many parameters are being maintained and recorded as a function of time, including heat transfer rate, acid dew point, temperature, and, on some specially instrumented tubes, the tube wall thickness. The rate at which the last parameter changes with time provides a measure of the corrosion rate. Results of this project are expected to be available in the latter half of 1984.

## RP982-19: Screening Study for Corrosion Inhibitors in $SO_2$ Removal Systems.

It is well established that corrosion of metals can often be inhibited by the addition of quite small amounts of a chemical species that would not naturally be present. The feasibility of using inhibitors to control corrosion in $SO_2$ scrubbers was addressed in this small laboratory study. The results indicated that none of the 26 compounds evaluated (see Table 6) inhibited corrosion of C-steel well enough to consider its use in scrubbers. However, one compound (N-lauroylsarcosine) and several of its analogs were found to inhibit general corrosion of Type 304 and Type 316 stainless steels. More important, these compounds greatly increased the resistance of the stainless steels to pitting attack. Since pitting and other forms of localized corrosion are responsible for the failure of many scrubber components, the identification of this pitting inhibitor was considered most significant.

TABLE 6. COMPOUNDS TESTED AS POTENTIAL CORROSION INHIBITORS IN RP982-19

3,3',4,4'-Benzophenone tetracarboxylic dianhydride
benzotriazole
S-(t-butyl)-thioglycolic acid
α-cyclohexylaminobutyric acid
N-cyclohexyl-2-pyrrolidone
N-cocoalkyl-2-pyrrolidone
1-ethylquinolinium iodide
gelatine
potassium thiocyanate
linear (C-12) alkyl sulfonate
S-lauryl thioglycolic acid
sodium benzoate
sodium diethyldithiocarbamate
sodium dimercaptothiadiazole
N-lauroylalanine
N-lauroylglycine
N-lauroylsarcosine (sodium salt)
N-octanoylsarcosine
N-stearolysarcosine
octylamine
di-triethanolammonium dimercaptothiadiazole
N-formylpiperidine
N,N,N',N',2-pentamethyl-1,2-propanediamine
phenylthiourea
sarcosine
tetraethylammonium toluenesulfonate

EPRI plans to fund additional work to determine the feasibility of using corrosion inhibitors in $SO_2$ scrubbers. This work will confirm and extend the results obtained in RP982-19

### RP1871-10: Corrosion Inhibitors for FGD Systems

This project is due to commence early in 1984 and, as mentioned above, its objective is to evaluate further, the feasibility of using corrosion inhibitors in $SO_2$ scrubbers. Candidate inhibitors will also be assessed for their effect on the scrubber process ($SO_2$ removal).

## RP1871-11: Characterization of Ceramic Materials for Electric Power Plant Applications

Ceramic materials have been used quite often in FGD systems as liner materials on C-steel support structures. They are particularly useful in areas where erosion is a potential problem, but some ceramics (such as acid resistant bricks) have been used to line stacks and other scrubber components where corrosion, not erosion, has been of prime concern. There are disadvantages of using conventional ceramic liner materials. For instance, they are normally quite bulky and, as a result, cannot be retrofitted in some narrow section locations, such as venturi throats; and, rapid changes in temperature can generate sufficiently high stresess in ceramics that they will crack and spall.

Some of these disadvantages can be avoided by using relatively thin prestressed ceramic tiles. Here, the tiles are carefully designed and assembled to support an initial compressive stress which counterbalances the stresses induced in service by rapid temperature changes. This concept has so far seen only very limited application: prestressed SiC tiles have been successfully retrofitted in one venturi prescrubber that had experienced serious erosion problems, but more widespread application is limited by our lack of knowledge of the physical and mechanical properties of the ceramic materials at the temperatures of interest. The objective of RP1871-11 is to generate such information for selected ceramic materials so that prestressed ceramic components can be incorporated into critical areas of FGD systems as needed. This project is due to start within a few months.

## RP2248-2 and RP2248-3: Materials Failure Causes In FGD Systems

There is no doubt that materials used in FGD systems have failed to perform their intended function on more than a few occasions. There is ample documented evidence (see RP982-14 and RP1871-3, for instance) that metals and nometallic materials can corrode, degrade, crack, and erode, and that coatings can disbond or degenerate. However, it is also apparent that much of the information available is inconsistent: a material that has performed well in one scrubber is reported to fail miserably in another scrubber operating under supposedly identical conditions. Furthermore, while the type of failure has often been documented (stress corrosion cracking, pitting, disbonding, etc.), there has seldom been any attempt to determine the cause of failure. For instance, Type 316 stainless steel may have given excellent service for several years in a scrubber environment containing 500 $g/m^3$ chloride, but because of an unusual upset condition (e.g. the temperature jumps from the normal 50°C to 100°C), the stainless steel suffers extensive pitting. The root cause of this failure is the upset condition but, unless such information is reported, a subsequent review of the available information may suggest that Type 316 stainless steel cannot be used safely in scrubber environments containing 500 $g/m^3$ chloride.

Consequently, EPRI initiated two projects recently (RP2248-2 and RP2248-3) which are designed to investigate and report the true causes of the failures of metals, coatings, and linings in FGD systems. It is hoped that these investigations will help avoid the apparent conflicts and inconsistencies in the literature that have developed in the past.

## SUMMARY

Over the last four years, EPRI has initiated many research projects to identify materials degradation problems in FGD systems and to develop solutions to those problems. During this period, our understanding of the mechanisms of degradation has improved and, with this understanding has come the ability to simulate scrubber conditions more accurately in the laboratory. However, the scrubber industry is still young and its problems plentiful. Materials scientists and corrosion engineers will play an important role in the future development and success of FGD systems.

## ACKNOWLEDGMENTS

The author wishes to thank S. Dalton, C. Dene, R. Rhudy, and D. Stewart of EPRI for reviewing this paper and for making many useful suggestions.

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4. G. H. Koch, J. A. Beavers, and B. C. Syrett, "Experimental Evaluation of Alloys and Linings of Simulated Duct Environments for a Lime/Limestone Scrubber," Paper No. 197, NACE Annual Conference, Houston, Texas; National Assoc. of Corrosion Engineers, Houston, Texas (1982).

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# SIMULTANEOUS DESIGN, PLANNING, AND MATERIALS OF CONSTRUCTION SELECTION FOR FGD SYSTEMS

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## ABSTRACT

Processes and systems designed for emissions control from fossil fuel fired boilers for electric generating stations are many and varied as are the choices of materials of construction. Good performance and efficiency of operation and maintenance of flue gas desulfurization systems can be enhanced by the simultaneous selection of the process, the design, and the materials of construction of the system. The wet lime and limestone systems are the dominant processes for removal of sulfur dioxide from coal fired boiler flue gases and will remain so for the next several years, based on EPA surveys. The choices of material include carbon steel, coatings and linings that can be applied over carbon steel, a wide range of alloys that can be used in place of lined carbon steel, and various nonmetallic materials. It is the purpose of this paper to discuss the corrosion and abrasion resistance of these materials and to show how each may be most advantageously used in the design of an FGD system.

## INTRODUCTION

The composition of flue gases produced during the combustion of coal vary widely. The major polluting impurities in coal are sulfur, chlorine, and non-combustible inorganic matter which appear in flue gas as sulfur dioxide, hydrogen chloride, and flyash respectively. Federal and state regulatory agencies have enacted stringent legislation requiring utilities to remove the major portion of flyash and the oxides of sulfur from flue gas before it can be returned to the atmosphere. The use of large scale desulfurizing equipment became important in the early 1970's.

The early operating problems were solved and FGD technology gradually improved due in part to:

- fundamental research done at Research Triangle Park, Battelle Institute, the University of Texas at Austin, and the University of North Dakota,
- process development work done at the Shawnee Test Facility, and at various pilot plants,
- engineering during the design of new FGD systems,
- tests performed at various full scale installations.

Good overall system performance has been achieved by properly selecting the process, the design, and the materials of construction. A utility must often invest many millions of dollars to design, install and operate an FGD system, so economic optimization of both process parameters and materials of construction are very significant.

The primary chemical pollutants produced during coal combustion are sulfur dioxide and sulfur trioxide; one or two percent of the total coal sulfur is usually converted to sulfur trioxide. The required degree of sulfur dioxide removal is determined by NSPS regulations, summarized by Stevenson(1). At the present time, the removal of sulfur dioxide is most commonly accomplished by a wet process in a multilevel spray tower, using lime or limestone as the alkali.

## PHILOSOPHY OF SYSTEM DESIGN

An FGD system is a chemical plant, and, as such, the materials of construction must be carefully selected to provide the maximum resistance to the system environment at the minimum cost. Site specific considerations such as the generating capacity of the power plant, and its geographic location, determine the type and quantity of coal burned, and therefore the amount of gas to be treated and the amount of sulfur to be removed. These parameters determine the physical size of the process equipment. Other regulations pertaining to the nature of the final disposal product, and the requirement for closed loop water balance, in conjunction with the chlorine content of the coal determine the concentration of dissolved solids in the scrubbing loop. Laslo and Chang(2,3) have discussed the effects of dissolved chlorides on FGD chemistry.

Sulfur trioxide condenses as very small droplets at the temperatures of the system inlet ductwork. These extremely fine sulfur trioxide droplets cannot be efficiently trapped in spray towers; they pass through the absorbers in the gas stream, and are deposited on the walls of the downstream equipment and ductwork. Sulfur trioxide particles which do not impinge on any surfaces leave the system with the stack gas. Sulfur trioxide condenses in the form of 40 - 60 percent sulfuric acid solutions at about 100 to 120 F to create extremely corrosive media. Pierce(4) has correlated much of the available data on sulfuric acid condensation (dew point). The results of his work are shown graphically in Figure 1.

Chlorine is a second chemical that causes corrosion problems in FGD systems. It is present in almost every coal; its concentration may be negligible or as high as 0.5 weight percent. Many FGD systems are designed based upon coals containing approximately 0.1 percent of chlorine. In colder climates, coal piles are often sprayed with dilute calcium chloride solutions to prevent freezing. Chlorine introduced in this fashion is identical to that introduced by naturally occurring chlorine. During and immediately after combustion, the contained chlorine is converted to hydrogen chloride gas which is removed in the wet scrubbing system. All chlorine compounds of interest are highly water soluble, and all of the absorbed chlorine must leave in the free-water fraction of the final product. Since most regulatory agencies require FGD systems to operate under closed loop water balance conditions, and many systems operate with forced oxidation to improve the disposal properties of the sludge, high concentrations of chlorides can occur in the circulating liquids.

The final process material that may create operating problems is the scrubbing slurry itself. In lime or limestone systems the slurry is a mixture of calcium sulfite, calcium sulfate, fresh alkali and flyash. In at least one successful operation, flyash is removed from the flue gas in a high efficiency venturi scrubber and the resulting flyash slurry is used to remove sulfur dioxide in a spray tower(5). The major material problem associated with the handling and pumping of these slurries is erosion in such system components as spray nozzles, pumps, agitators, and the absorption zone. In fact, the slurry exiting the spray nozzles may be likened to a wet sandblast.

## STATEMENT OF THE PROBLEM

It is the object of this paper to review the FGD process from the standpoint of materials of construction and to demonstrate how the proper material selection enhances FGD plant operation and economics. The major material problems that must be addressed are corrosion, erosion, thermal effects, and chemical imbalances such as plugging and scaling which can occur at various points in the system. A summary of how these problems affect the design and operation of

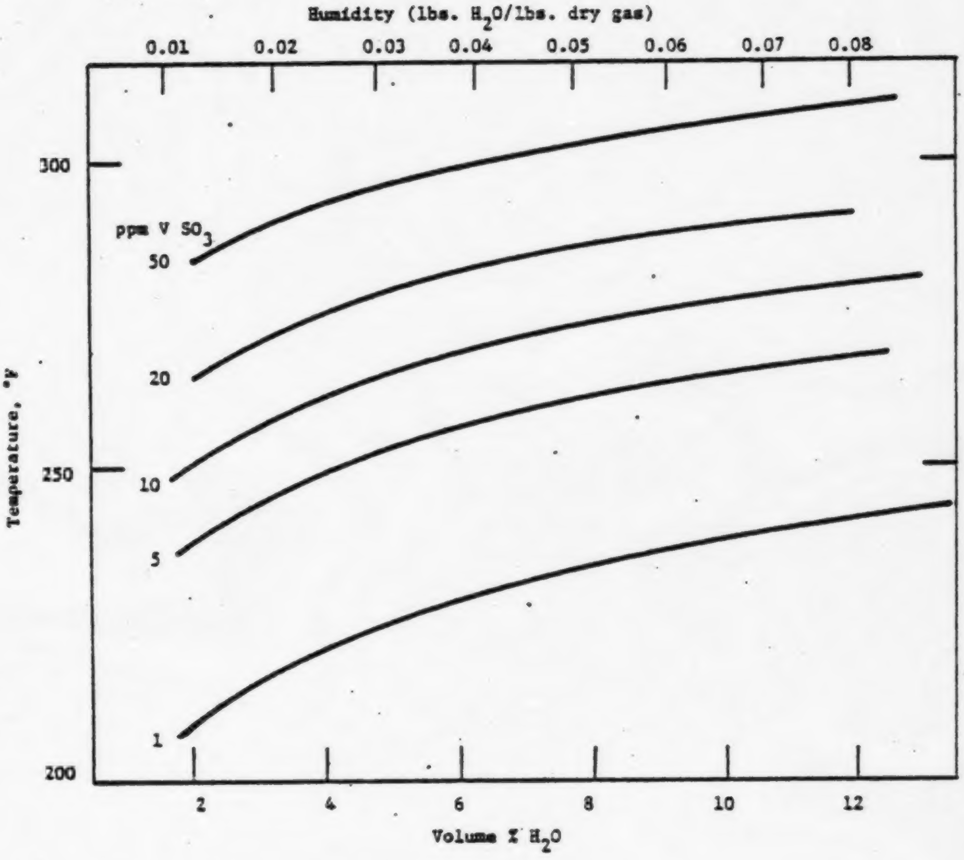

Figure 1: Sulfuric acid dew point in flue gas.

various system components is given in Table 1. A schematic flow diagram highlighting these problem areas is shown in Figure 2.

In choosing materials of construction for an FGD system, one must consider the corrosive and erosive nature of the process stream and the temperatures and temperature gradients to which the system components will be exposed. Chemical imbalances, although important in the overall system design, will only receive minor attention here.

## MATERIALS OF CONSTRUCTION

The choices of materials of construction for system components include base metal, such as carbon steel, carbon steel coated with various organic and inorganic coatings, and alloys. These are summarized in Table 2. Alloy compositions are listed in Table 3.

The following sections describe these materials.

### CARBON STEEL

The most extensively used material in FGD systems is carbon steel. It is used in hot, dry atmospheres, and in alkali environments where it needs no protection against corrosion. Carbon steel corrodes rapidly in wet or acidic environments.

### LINED CARBON STEEL

Lined, or coated, carbon steel economically overcomes many of the shortcomings of carbon steel.

#### Organic Linings

##### Flakeglass

Flakeglass filled vinylester and polyester resins are used in wet sections of FGD systems, such as the absorber vessel, the outlet ductwork, and various tanks. They provide economical corrosion protection with moderate erosion resistance. These liners cannot withstand high temperatures, and a reasonable amount of temperature control is necessary. These materials are usually specified because of their generally high reliability and low initial cost.

##### Rubber

Rubber linings are used where abrasion is the primary problem. They are most frequently used in scrubber

### TABLE 1
### SERVICE CLASSIFICATION OF FGD SYSTEM COMPONENTS

| | CORROSION | EROSION | THERMAL EFFECTS | CHEMICAL IMBALANCES |
|---|---|---|---|---|
| 1. Inlet Ductwork | M | N | M | N |
| 2. Absorber Inlet | S | M | M | S |
| 3. Absorber Body | S | S | M | S |
| 4. Mist Eliminator | S | M | M | S |
| 5. Absorber Outlet | S | M | M | M |
| 6. Outlet Ductwork | S | M | M | S |
| 7. Reheaters & Assoc. Ductwork | S | M | S | S |
| 8. Stack Breeching | S | M | S | S |
| 9. Alkali Tanks | N | M | N | N |
| 10. Recycle Tanks | S | M | M | N |
| 11. Slurry Piping | S | S | M | M |
| 12. Slurry Nozzles | M | S | M | M |
| 13. Dampers | S | M | S | S |

S =Severe problem; M =Minor problem; N =not usually a problem

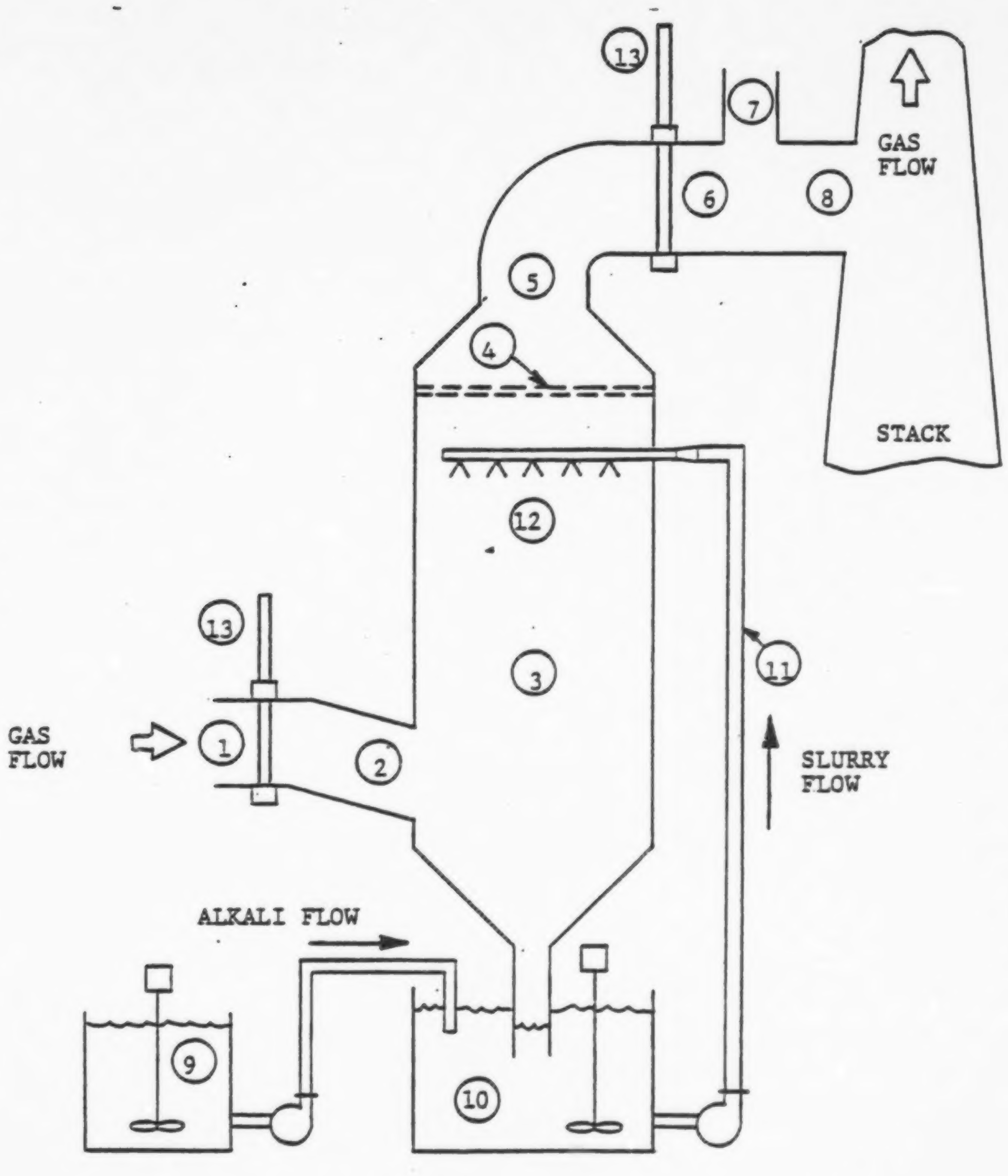

Figure 2: Schematic Flow Diagram of a Wet FGD System
Numbers in circles refer to Table 1.

# TABLE 2
## MATERIALS OF CONSTRUCTION

| | |
|---|---|
| I CARBON STEEL | 1.0* |
| II LINED CARBON STEEL | |
| A. ORGANICS | |
| a. Flakeglass | 2.0 |
| b. Vinylester | 2.0 |
| c. Natural Rubber | 2.5 |
| d. Neoprene | 2.8 |
| e. Chlorobutyl Rubber | 2.6 |
| f. Fluoroelastomer | 5.5 |
| B. INORGANICS | |
| a. Monolithics | 2.5-3.5 |
| b. Acid Brick | 3.1 |
| c. Borosilicate Block | 3.0 |
| III ALLOYS | |
| A. LOW ALLOYS | |
| a. 316L | 3.0 |
| b. 317L | 4.0 |
| c. 317LM | 4.5 |
| d. 255 | 4.0 |
| B. MEDIUM ALLOYS | |
| a. 20Cb-3 | 3.8 |
| b. 825 | 5.5 |
| c. 904L | 5.0 |
| d. JS-700 | 5.0 |
| C. HIGH ALLOYS | |
| a. G | 5.5 |
| b. G3 | 5.5 |
| c. 625 | 8.5 |
| d. C-276 | 9.0 |

See Table 3 for alloy chemical compositions

* Approximate Relative Installed Costs

## TABLE 3
## NOMINAL CHEMICAL COMPOSITIONS

| | Fe | Cr | Mo | Ni | Cu | C | Other | Approx. Relative Cost[6] |
|---|---|---|---|---|---|---|---|---|
| Carbon Steel | | | | | | | | 0.4 |
| **LOW ALLOYS** | | | | | | | | |
| 316L | Bal | 17 | 2.5 | 12 | - | 0.03[5] | | 1.0 |
| 317L | Bal | 19 | 3.5 | 13 | - | 0.03[5] | | 1.3 |
| 317LM[1] | Bal | 19 | 4.35 | 14 | - | 0.03[5] | | 1.4 |
| FERRALIUM alloy 255 | Bal | 25.5 | 3.5 | 5 | 1.7 | 0.04 | N-0.17 | 1.4 |
| **MEDIUM ALLOYS** | | | | | | | | |
| Alloy 20CB-3 | Bal | 20 | 2.5 | 35 | 3.5 | 0.07[5] | | 2.8 |
| UHB 904L[2] | Bal. | 20 | 4.5 | 25 | 1.5 | 0.02 | | 2.1 |
| JS-700[3] | Bal | 21 | 4.5 | 25 | - | 0.05 | Cb-0.3 | 2.1 |
| INCOLOY alloy 825 | 30 | 22 | 3.0 | Bal | 2 | 0.03 | | 2.9 |
| **HIGH ALLOYS** | | | | | | | | |
| HASTELLOY alloy G | 20 | 22 | 6.5 | Bal | 2 | 0.05[5] | W-1.0[5]<br>Cb+Ta-2.0 | 3.9 |
| HASTELLOY alloy G-3 | 20 | 22 | 7 | Bal | 1.5 | 0.007 | Co-5.0[5],<br>W-1.5[5],<br>Cb+Ta-0.5[5] | 3.9 |
| INCONEL alloy 625[4] | 5[5] | 21.5 | 9 | Bal | - | 0.10 | Cb+Ta-3.5 | 5.9 |
| HASTELLOY alloy C-276 | 5 | 16 | 16 | Bal | - | 0.005 | V-0.35[5], | 6.6 |

[1] Eastern Stainless Steel Corporation
[2] Uddeholm AB
[3] Jessop Steel
[4] Also CABOT alloy No. 625
[5] Maximum
[6] Equal weight basis

absorption zones, slurry piping, and slurry pumps. During construction, care must be taken when the steel substrate is prepared and the rubber lining is applied. The steel surface must be freshly cleaned and sandblasted.

Natural rubber is lowest in cost, easiest to apply, and has the highest degree of abrasion resistance. The drawbacks to using natural rubber are its higher flammability, and its lower resistance to oil. Oil, used in boiler startup and in flame stabilization, has not proven to be harmful, but if oil alone is used for fuel for extended period of time it may not be completely burned and may enter an FGD system via the flue gas and soften the rubber.

Neoprene rubber has improved fire and oil resistance but is more expensive to purchase and more difficult to apply. Neoprene has higher permeability and lower resistance to abrasion than does natural rubber. The applied cost of neoprene linings (per square foot) is approximately 20 percent higher than natural rubber.

Chlorobutyl linings are becoming increasingly popular in new construction and in replacements. Chlorobutyl rubber has lower permeability than does natural rubber. Its abrasion resistance is somewhat lower than natural rubber; its oil resistance is higher than that of natural rubber and lower than that of neoprene. The applied cost of chlorobutyl linings (per square foot) is approximately 10 percent higher than natural rubber.

Rubber lined carbon steel is the most commonly used material of construction where abrasion is a problem.

### Fluoroelastomer

Fluoroelastomer linings are not usually used in absorbers. They have been successfully used in outlet ductwork where temperatures may be high due to reheat requirements. Fluoroelastomers are usually applied by spraying. The applied cost of fluoroelastomer linings (per square foot) is approximately 300 percent higher than natural rubber. The thickness of fluoroelastomer linings is only about 20 percent of rubber linings.

## Inorganic Linings

Inorganic linings are more expensive than organic linings, with the exception of the fluoroelastomers. They are used in parts of the system where corrosion protection is required and where the temperatures are too high for the organics. An important application of inorganic linings is in outlet ductwork, downstream of the reheater. They are applied to the base steel as either monolithic or as brick/mortar linings. Monolithic linings are gunned onto the steel. A steel wire mesh, anchored to the base steel, is required for support. In areas where these linings become wet, an impervious membrane is required at the steel interface. A relatively large number of proprietary monolithic lining materials are available for FGD applications. These materials are quite heavy; many are not resistant to strong acids that may exist in the systems.

Acid brick/mortar has good corrosion and abrasion resistance and is used in some prescrubbers, where erosive slurries wear away most coatings. A membrane is necessary to protect the substrate. Many systems are designed with a layer of acid proof brick to protect the bottoms of various tanks against physical damage while being cleaned. Acid brick is resistant to the acidic environments in wet stacks (no reheat).

Borosilicate glass blocks are being used to line outlet ductwork in several installations. This material has the added advantage of being a good thermal insulator and external insulation is unnecessary. The mortar must be selected to withstand the environment. A membrane is necessary to protect the substrate.

The major problems associated with inorganic linings are:

- Cracks often develop during the curing of linings and mortars.
- Corrosive gases ($SO_2$, $SO_3$, HCl) can diffuse through lining and mortars requiring impervious membranes to protect carbon steel substrates.

## PLASTICS

Fiberglass Reinforced Polyester (FRP) is noted for its very good corrosion resistance and moderate temperature resistance. Solid FRP construction is used in piping systems, for small tanks, mist eliminators, and stack liners. FRP flues are used in several stacks.

## CERAMICS

The use of ceramic materials has been limited to spray nozzles. They are highly successful there, and the success justifies the high initial cost.

## ALLOYS

Alloys are chosen because their physical or chemical properties are superior to those of the component metals in such areas as strength, and corrosion resistance. Alloys have been classified "low", medium", and "high" according to their resistance to corrosion and approximate cost range. These are listed in Table 3; registered trademarks are listed in Table 4.

The low alloys include the austenitic (or 300 series) stainless steels and FERRALIUM ® Alloy 255, a duplex (austenitic-ferritic) stainless steel that contains less nickel, about the same amount of molybdenum, and more chromium than austenitic stainless steels. Alloy 255 has seen wider application in Europe and is becoming increasingly popular in FGD applications in the USA.

The baseline corrosion resistant alloy for FGD systems is 316L, for the following reasons:
- generally good corrosion resistance,
- easy to clean,
- low carbon levels minimize welding problems,
- it is readily available at moderate cost.

316L has been successfully used in scrubber vessels, internal components and reheater components, where temperatures are below 140 F, pH's are above 5.5, and chloride levels are below 1,000 ppm. In lower pH or higher chloride environments, 316L is vulnerable to corrosion, particularly when it is used as shell material or structural members. Severe corrosion has been observed between any gypsum scale that might form, and the metal. 317LM (4.0% Mo minimum) is used for slightly more severe conditions. A few utilities have selected Alloy 255 to replace 316L and 317LM parts that have undergone pitting corrosion.

Medium alloys are used in areas where the corrosive environments are more aggressive. They are characterized by generally higher chromium, molybdenum, and nickel contents than are contained in the low alloys. Some alloys in this class have small amounts of copper added for higher resistance to sulfuric acid.

High alloys are used when chloride and/or sulfuric acid concentrations are high, pH levels are low, or when temperatures are high. High alloys differ from low and medium alloys in that they are nickel, rather than iron-base alloys. They contain higher molybdenum and generally higher chromium levels than do the medium alloys.

The Limestone Users Handbook(6) states that:

"316L SS is finding widespread use as a material of

## TABLE 4
## REGISTERED TRADEMARKS

FERRALIUM is a registered trademark of Bonar Langley Alloys, LTD.
20-Cb-3 is a registered trademark of Carpenter Technology Corp.
INCOLOY is a registered trademark of International Nickel Co.
INCONEL is a registered trademark of International Nickel Co.
HASTELLOY is a registered trademark of Cabot Corporation
CABOT is a registered trademark of Cabot Corporation
STEBBINS is a registered trademark of Stebbins Engineering and Manufacturing Company

> construction, however, under certain conditions of scrubber liquor pH, temperature, and chloride content, this alloy can undergo localized attack. Under these more stringent conditions, nickel-base alloys with higher molybdenum and chromium content are superior to 316L stainless steel. It has been shown that resistance to stress-corrosion cracking is achieved with higher nickel contents because nickel accelerates repassivation of the metallic surface(7). Although more expensive initially, these high-grade alloys may be economically justified for use in certain severe scrubber environments.
>
> The beneficial effect of molybdenum content is shown in Figure 3 which indicates that the resistance of alloys to pitting and crevice corrosion generally increases as the molybdenum content increases (8). Moreover, molybdenum content alone does not ensure resistance to localized attack."

Chromium content is also important as shown by the Shawnee test results plotted in Figure 4(8) and confirmed by others(9). These data indicate that the resistance of various alloys to localized corrosion is a function of the combined molybdenum and chromium content.

Primary variables affecting the choice of alloys are temperature, pH and the concentration of dissolved material (especially chlorides, and sulfuric acid). Table 5 shows the approximate limits for alloys that have proven successful in FGD applications. This table was developed from Cabot's experience derived from over 150 field corrosion test racks, and the results of several major surveys of materials of construction in operating systems(10,11). It is emphasized that this table is only a guide.

## FGD SYSTEM COMPONENTS

This section discusses several system components in detail, describes some material problems, and indicates which materials are generally used in the particular service.

### Inlet Ductwork

The inlet ductwork must be able to withstand typical flue gas temperatures and occasional excursions due to such causes as air preheater failures. They are normally fabricated of carbon steel and can be insulated to prevent uncontrolled cooling and possible sulfuric acid condensation.

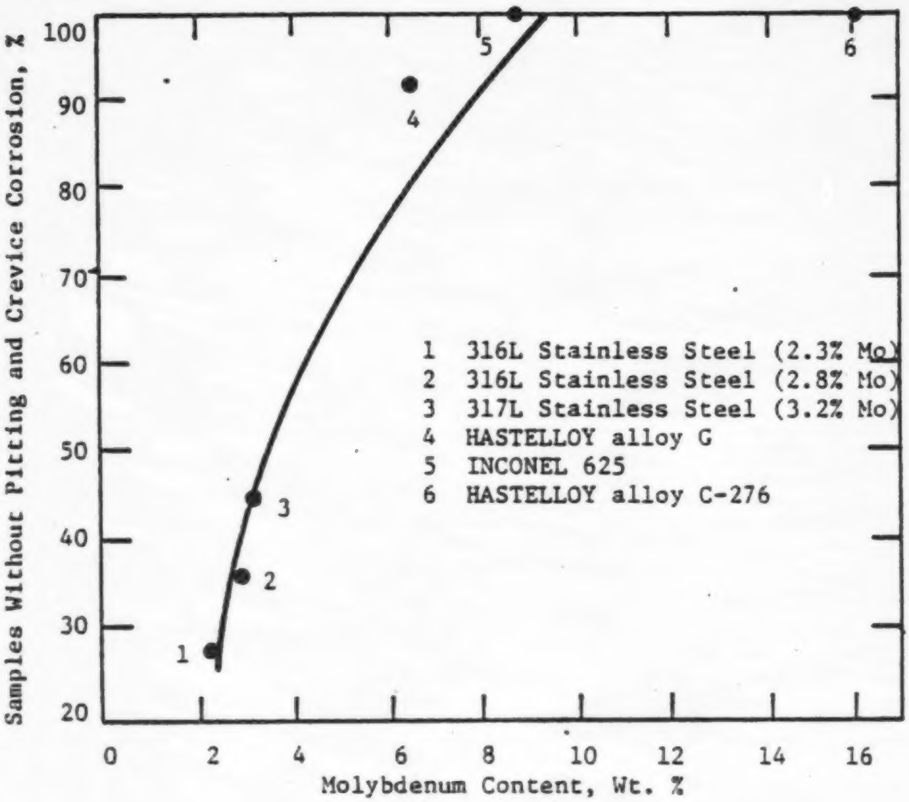

Figure 3: Effect of molybdenum content on resistance to pitting and crevice corrosion.

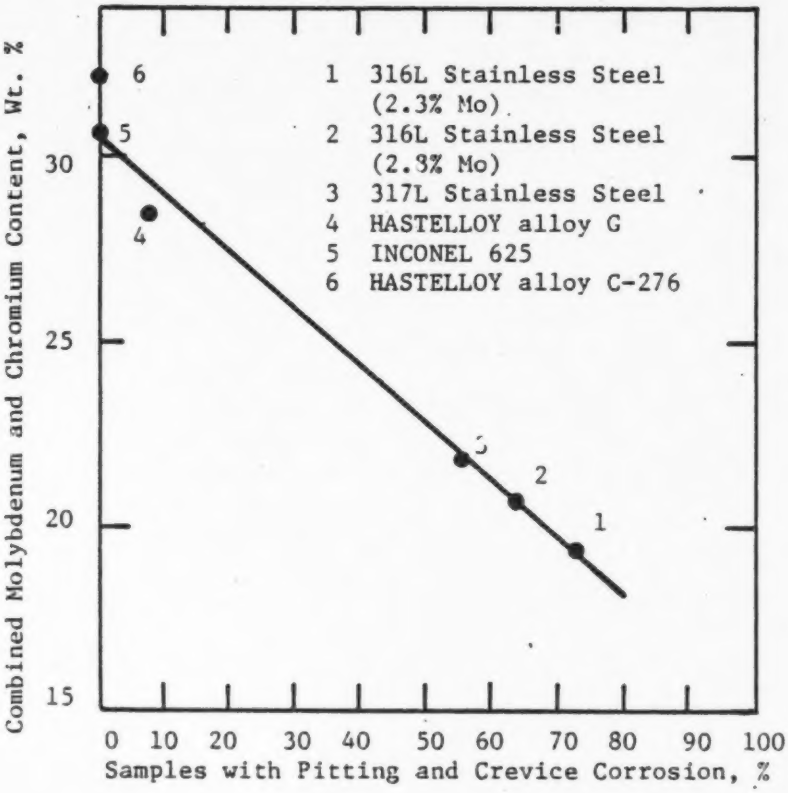

Figure 4: Effect of molybdenum and chromium content on corrosion resistance (Shawnee tests).

## Table [illegible]

## Service Application Guidelines Based on Cabot Test Results

| Service Condition | 316L Stainless Steel | FERRALIUM alloy 255 | HASTELLOY alloy G/G-3 | CABOT alloy No. 625 | HASTELLOY alloy C-276* |
|---|---|---|---|---|---|
| Maximum Temperature, °F | 150 | 150 | 160 | 160 | 225 |
| pH | Over 5.5 | Over 4.5 | Over 3.5 | Over 3.5 | Over 2.0 |
| Chloride Content, ppm | Under 1500 | Under 3000 | Under 5000 | Under 8000 | 30,000 |

* Alloy C-276 has been used successfully up to at least these levels.

## Absorber Inlet

This is the interface between the inlet duct and the body of the absorber. It is subjected to thermal stresses and the most aggressive corrosive environment in an FGD system. Gases enter this section at temperatures varying between their normal values of 250 to 350 F, and upsets which may be as high as 700 or 800 F; and leave at or near their saturation temperatures which vary between about 110 and 150 F, depending on gas inlet temperature, humidity, and altitude. In several systems, the absorber inlet sections serve as presaturators, where large volumes of FGD liquids or slurries, sprayed into the gas, quench it to its saturation temperature. Other systems provide liquid sprays to flush the walls and prevent solids from building up at the wet/dry interface; the gases are only partially saturated here. Other systems use carefully constructed inlet vanes to maintain stable gas velocity profiles, and still others provide no protection at all.

The high temperatures and temperature gradients at the entry section of the absorber inlet preclude the use of most organic linings. Inorganic linings can, and have been, used here but the use of high and medium alloys is preferred. This region of the ductwork where the most severe temperature problems and the most agressive corrosion environments exist is usually quite small, and the additional cost of the alloy parts is justified by the trouble free operation that will ensue. Alloys are not subject to the major defficiencies of inorganic linings which are delamination from the base steel and leakage of corrosives to the base metal. The absorber inlet should be designed to prevent accumulation of solid materials at the wet/dry interface between the ductwork and the absorber, and to avoid stagnation zones, where pools of absorber liquids can accumulate and cause corrosion.

## Absorber Body

The absorber body is the largest and costliest component of the FGD system and must be protected from corrosion, erosion, and thermal and chemical effects. Of these, the thermal effects are usually the smallest.

The majority of FGD absorber bodies are constructed of either organic lined carbon steel or low alloys. The "EPA Utility FGD Survey" (C1110) reports that organic lined carbon steel is used in approximately 75% of all FGD absorbers. The alloy absorbers, almost exclusively 316 or 316L, have only been successful when exposed to low concentrations of corrosive materials -- notably chlorides. Alloy absorbers must be designed with a minimum of sites for corrosive materials to accumulate. Alloys have the advantage of ease of repair and modification; penetrations and welds can be made with a minimum of difficulty. Organic lined steel absorbers do not have the same limitations on corrosive materials or physical design but linings must be periodically inspected and repaired as necessary.

It is also recognized that different locations within lined FGD absorbers are exposed to different corrosive and erosive environments. Absorbers are therefore designed with different materials at different points. The spray zones, subjected to the severest abrasive conditions, are usually rubber lined. The direction of the recycle sprays must be carefully adjusted to minimize impingement on, and erosion of, other internal components, such as walls, beams and pipes.

The components of the absorber not directly exposed to the abrasive action of the recycle sprays are often coated with glass filled polyester resin. This material has equivalent corrosion resistance and is easier to apply and is less expensive than rubber. Alumina filled resins may be used in applications involving high fluoride concentrations.

A well designed steel absorber shell is usually covered with at least two different linings, typically rubber and flake filled polyester. Direct chemical bonding between such materials is not usually successful, and the absorber shell should be made of flanged sections, one covered with rubber, bolted to another covered with polyester. The linings are extended oustide of the absorber body and completely cover the flange faces to assure leak tight joints. This is shown schematically in Figure 5.

A small number of ceramic tile absorbers are being successfully operated.

Chemical phenomena include $SO_2$ removal, limestone dissolution, gypsum desupersaturation, and system pH, and have been studied at length and reported in various symposia and similar learned publications.

Mist Eliminators

Mist eliminators are generally constructed in two stages. In the Peabody system, the first, or lower stage, is a perforated interface tray that acts as a bulk entrainment separator. It is continuously washed with a combination of process slurry and makeup water. Despite the potentially

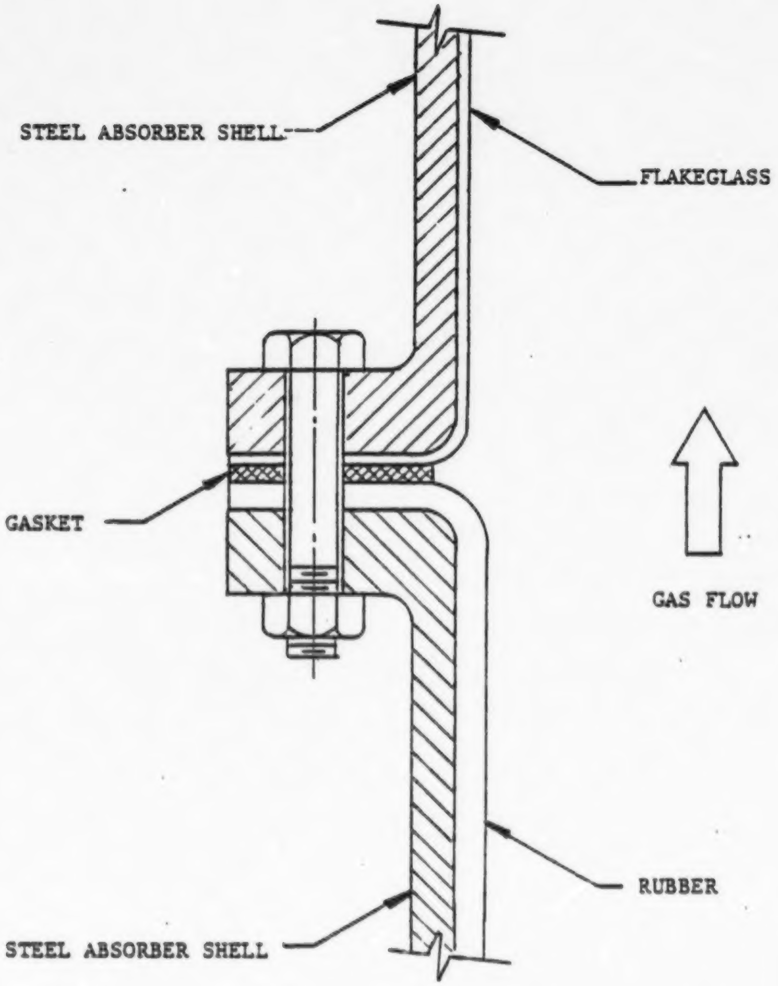

Figure 5: Mechanical Joint for Dissimilar Linings

corrosive environment, successful operation with 316L stainless steel interface trays has been achieved since it is not a structural member and is continuously flushed. In applications where very high chlorides are expected, higher alloys such as Alloy G have been specified.

The second, or upper mist eliminator stage, is usually a set of chevrons. The major problems here are thermal deformation of the blades, and slurry deposition and scaling within the chevron passages. The thermal deformation has been attributed to the diffusion of hot flue gas from an outlet or bypass duct into the top of an absorber module that is being taken off line, and where the inlet damper is closed before the outlet damper. The problem has been successfully solved by altering the damper startup/shutdown sequences and by replacing the somewhat fragile thermoplastics with more rugged FRP or Alloy parts. Solids deposition and scaling are potentially serious but these have been overcome by the introduction of a sufficient flow of water to remove any deposits before they can be converted to gypsum and adhere to the surface. The absorber shell in this area is carbon steel with a flakeglass filled polyester resin lining.

## Absorber Outlet

The absorber outlet may experience a more highly corrosive environment than the body of the absorber but abrasion is not a problem. The corrosive environment is being created when residual sulfur dioxide or sulfur trioxide is absorbed by condensed water and not neutralized by the FGD alkali. This condition may be exascerbated by the presence of chlorides.

Despite the corrosive nature of the liquids here, corrosion is usually minimal because of the rather low (saturation) temperatures, the suitability of the linings, and the vertical arrangement of the equipment which minimizes accumulations (especially important in alloy vessels). The same materials of construction used in the mist eliminator sections are used here: the absorber shell is carbon steel with a flakeglass filled polyester resin lining.

## Outlet Ductwork

The outlet ductwork is subjected to the same conditions as the upper sections of the absorber but corrosion is potentially more severe because of the horizontal position of the ductwork. Lined steel is the most frequently used material of construction here.

## Reheaters and Associated Ductwork

Many FGD systems are designed with reheaters to increase gas buoyancy and velocity within the stack. Outlet ducts, prior to reheat or bypass zones are carbon steel with flakeglass filled polyester resin linings. For the hotter zones, monolithic inorganic linings, borosilicate glass blocks, and fluoroelastomers are used to protect carbon steel ducts. Alloys are used as both corrosion resistant linings for carbon steel, and as free standing structural materials in the ductwork at several installations. The 300 series stainless steels often undergo pitting corrosive and, in some systems even meduim alloy are inadequate.

Reheat is accomplished either directly or indirectly. In direct heating a row of heated tubes is placed in the path of the scrubbed flue gas. The first few rows of tubes are prone to scaling due to the evaporation of entrained water droplets and deposition of the solid material on the tube surface. The tube surfaces may also be moist due to the presence of residual liquid, and thus an area of potentially high corrosion can be established. Unfortunately good heat transfer requires bare metal surfaces so the tubes cannot be coated with a protective material. Solid deposits are removed from the surfaces with soot blowers. Tubes are generally constructed of high alloys at the reheater inlet and lower alloys, or even carbon steel for the remaining tubes.

In indirect heating, a gas, usually air, is externally heated and then mixed with the scrubbed flue gas to bring the mixed temperature up to the desired point. A mixing device is required to thoroughly mix the hot reheat gas with the cooler scrubbed gas. The gas mixing device has many of the same corrosion problems as the absorber inlet section where the most aggressive corrosive environments and largest temperature gradients exist. The mixing baffle is usually constructed of medium or high alloys. Indirect reheating is more commonly used than is direct reheating.

A variation of indirect reheating is "bypass reheating". This is usually economically attractive in systems burning low sulfur coal and requiring low (approximately 70%) overall $SO_2$ removal. The absorbers are operated at high efficiencies and a portion of the flue gas is bypassed and mixed with the scrubbed gas to increase the temperature. The reheat gas is not scrubbed and carries with it the sulfur dioxide, sulfur trioxide, and hydrogen chloride present in the original flue gas. This creates more serious corrosion problems for the ductwork and the gas mixers. The ductwork is usually lined as mentioned above and the mixing baffle is made of a higher alloy. Another application of bypass reheat involves using a very small amount of air preheater inlet gas (at about 800 F) to heat scrubbed gas. A small electrostatic precipitator removes particulate from the reheat gas prior to mixing.

Fluoroelastomers appear to be successful in outlet and reheat ductwork but experience is limited.

Reheaters generally employ inorganic linings over carbon steel for the ductwork, and medium and high alloys for the gas mixer.

## Stack Breeching

If neither reheat or bypass gas is introduced, flakeglass linings are acceptable. If the design requires reheat, higher temperatures preclude the use of organic linings. Inorganic linings have been used with some success, and considerable attention is being directed towards the use of alloys. Solid FRP flues are used in a number of installations. An alloy flue is used in at least one installation.

## Alkali Tanks

Alkali storage tanks are usually made of unlined carbon steel.

## Recycle Tanks

Recycle tanks, located at the base of absorber modules, provide the necessary residence time for the FGD chemical reactions. The preferred material of construction here is carbon steel with linings of either glass filled polyester or vinylester resin and an acid brick covered base. When agitation is required, rubber covered agitators are used.

### Slurry Piping

Both rubber lined steel and FRP pipe are used for slurry service. Rubber lined and rubber covered pipe is used inside the absorber vessels. Rubber lined pipes are expensive but are extensively used because they combine abrasion and corrosion resistance, and are very reliable.

### Slurry Nozzles

Nitride bonded silicon carbide is almost exclusively used for slurry nozzles. There have been no reports of failures due to either abrasion or corrosion with this material.

Applications that require water sprays, such as in mist eliminators and certain presaturators, employ cobalt-base wear resistant alloy nozzles. This minimizes abrasion due to small amounts of suspended solids.

### Dampers

Dampers are subjected to the same environments as the ducts in which they reside. Blades are carbon steel or low alloy in the inlet ductwork, and medium or high alloy in the outlet ductwork. The choice of materials is site specific and depends upon such considerations as temperature and sulfur trioxide level of the incoming gas, and temperature and sulfur dioxide, sulfur trioxide, and chloride contents of the absorber outlet gas. Damper seals are usually fabricated of high alloys, such as 625 and C-276 for both inlet and outlet dampers.

## EXPERIENCE

This section describes several case histories where materials of construction listed in Table 2 have been used.

### ORGANIC COATING APPLICATIONS

Minnesota Power and Light Company, Clay Boswell No. 4, Cohasset, Minnesota is a 550 MW coal-fired plant. The plant burns 1.0% sulfur Montana coal. A lime/alkali flyash FGD system that operates in a closed water loop mode removes 90 percent of the $SO_2$ from the flue gas. Reheat is supplied by bypass gas. Operations commenced in April 1980. Extensive use of non-metallic coatings over carbon steel was made in this system. The venturi is lined with natural rubber in wetted areas. The inlet section of the venturi which receives the hot flue gas and directs it to the orifice area is carbon steel and inorganic lining. The absorber vessel is fabricated in two sections. The absorption zone is lined with natural rubber. The mist elimination section above the absorption zone is lined with polyester flakeglass. The internal spray headers are carbon steel rubber lined, and rubber covered. The outlet ductwork downstream of the absorber has a vinyl ester flakeglass lining. The reheater mix zone is 316L. The materials of construction selected for this unit have performed satisfactorily. A problem was initially experienced with the rubber lined venturi vessel wall. The very high swirling velocity of the gas/slurry mixture leaving the venturi orifice eroded the rubber lining. The problem was solved by the installation of straightening vanes in the inlet duct.

## RUBBER COATINGS AND ALLOY APPLICATIONS

Alabama Electric Cooperative, Tombigbee Station, Units No. 2 and No. 3, Leroy, Alabama, are each 255 MW units that burn 1.8 percent sulfur (maximum) coal. The limestone FGD system scrubbing liquor contains about 800 ppm of chlorine and the pH is normally maintained at 5.8. Organic coatings over carbon steel are used extensively in this installation. Natural rubber and flakeglass filled polyester resin linings are used in the absorber and recycle tanks; and a fluoroelastomer lining is used in the outlet ductwork. The absorber inlet is INCOLOY ® Alloy 825. The system has been in service for more than four years. Only minor repairs have been necessary.

Solids deposition in the absorber inlet ducts and the resulting corrosion is avoided by the installation of deflector baffles around the perimeter of the inlet duct to divert the flow of gas away from the wall. Fan shaped sprays located behind the deflector baffle deluge the duct wall. The duct is inclined so that the liquids drain into the body of the absorber.

South Mississippi Electric Power Association, R. D. Morrow, Sr. Plants (2 units, 190 MW each), Purvis, Mississippi uses a limestone process with a closed water loop. The plant burns 1.1 percent sulfur coal, and uses bypass gas to reheat the scrubbed gas. The gas temperature in the outlet duct and the stack breeching is above 200 F, which is higher than that in most other plants. A scale/sludge buildup, a foot or more thick, occurred on the inlet duct floor. Samples of this scale have been analyzed and found to contain high levels of chlorides and fluorides. A history of the severe corrosion problems and the materials used in an effort to combat these corrosion problems at this plant has been reported by Froelich and Ware(13). Rubber lining in the upper section of the absorber and the breeching between the top of the absorber and the outlet duct, and

HASTELLOY ® alloy G in the lower section of the absorber have proven to be satisfactory materials for those areas. Areas with the most stubborn corrosion problems have been the floor of the inlet duct and portions of the outlet duct. Based on corrosion tests conducted in the outlet duct for one year, the results of which are summarized in Table 6 and detailed elsewhere(14), HASTELLOY Alloy C-276 was selected for the inlet duct floor material and for use in the most severely corroded areas in the reheater section of the outlet duct.

The alloy C-276 was installed nearly three years ago. To date, only minor corrosion has been observed on the inlet duct floor and no corrosion is evident in the outlet duct.

## ALLOY APPLICATIONS

Southern Indiana Gas and Electric, A. B. Brown No. 1, West Franklin, Indiana is a dual alkali process with a closed loop water system. The fuel is a bituminous coal with 2.8 to 3.9 percent sulfur and 100 to 800 ppm chlorides. HASTELLOY alloy G was selected for two absorber tower disc components and two bottom spargers. Each contactor consists of a disc and doughnut, approximately 30 ft. in diameter. The initial startup was in April 1979. An inspection 4 years later revealed no corrosion.

The Northern Indiana Public Service Company, Dean H. Mitchell Station No. 11, Gary, Indiana, used a Davy McKee/Wellman Lord $SO_2$ recovery process with an Allied Chemical Corporation reduction process to reduce the $SO_2$ to 99.9 percent pure sulfur. These combined processes eliminated the need for sludge disposal. The plant burned coal with 3.5 percent sulfur. The absorber was constructed of STEBBINS ® tile. The orifice contactor and bottom supports of the absorber trough were made of HASTELLOY alloy C-276 and the outlet duct of HASTELLOY alloy G. This demonstration plant discontinued operation after running seven years, and was placed in the standby mode. Examination of the tile and the HASTELLOY alloy components after shutdown showed that they were essentially free of corrosion. The tile components were trouble free for the duration of the test.

Montana Power Company, Colstrip No. 1 and 2 (360 MW each), Colstrip, Montana has plate type stack gas heaters fabricated of HASTELLOY alloy G and CABOT ® alloy No. 625 plate type stack gas reheaters. These reheaters have performed satisfactorily with no corrosion problems since startup (No. 1, Nov. 1975; No. 2 Oct. 1976). The same combination of alloys has been chosen for the new power plants, Colstrip No's. 3 and 4, scheduled for startup in 1983

## TABLE 6
## RESULTS OF CORROSION TESTS AT SOUTH MISSISSIPPI

| ALLOY | REMARKS |
|---|---|
| Alloy C-276 | No localized corrosion |
| Alloy No. 625 | Weld metal pitting |
| Alloy G-3 | Moderate pitting in weld, light in base metal |
| Alloy G | Moderate pitting in weld, light in base metal |
| JS-700 | Moderate pitting |
| Alloy 255 | Moderate pitting |
| 904L Alloy | Heavy pitting |
| 317L Stainless Steel | Heavy pitting |
| 316L Stainless Steel | Heavy pitting |

and 1984, respectively.

Central Illinois Public Service Company, Newton No. 1, Newton, Illinois has a dual alkali closed water loop FGD system. The plant burns Southern Illinois coal with 2.8 - 3.2 percent sulfur (4.0 percent maximum) and 0.2 percent chlorine. The scrubbing liquor contains 15,000 to 18,000 ppm chlorides and the pH is maintained at 6.5. The system has four absorber towers each with a 22.5 foot diameter by 2 ft. high precooler ring at the top where the hot (approximately 325 F) unscrubbed gases enter and are quenched. The ring and spray quench system and other internals are made of HASTELLOY alloy C-276. Corrosion of these components has not been a problem in the four years of operation of this system.

## FUTURE TEST WORK

Cabot Wrought Products Division and Peabody Process Systems, Inc. have joined forces with three major utilities; NYSEG, Seminole, and Santee Cooper; for an extensive experimental survey of the corrosion resistance of various materials under actual field conditions. The three utilities are burning different coals which will provide three distinctively different corrosion environments.

Coupon racks have been designed by Peabody and built by Cabot. They will be installed prior to plant startup, at selected locations within the FGD system. Operating data, such as temperature, pH, and chloride levels, will be monitored by Peabody and by the utilities; and Cabot will analyze the samples in their research laboratories. The test racks will be examined after 12 and 24 months of exposure. Cabot and Peabody will jointly publish the results of this investigation.

## SUMMARY

This section highlights the preferred materials of construction from the large number of choices available.

The recommended material of construction for inlet ductwork is carbon steel. The recommended material of construction for the absorber inlet is a medium alloy because it can withstand both the thermal and corrosive environments. The physical design must prevent solids from building up. Carbon steel with one or more organic linings is the preferred material of construction for the absorber. Natural rubber is recommended for the absorption zone, the pump linings, and the internal slurry piping, which should be lined and covered. If oil firing is a major factor then neoprene rubber is preferred. Flakeglass filled polyester has proven satisfactory for the upper and lower sections of the absorber and the outlet ductwork, and is recommended there. The mixing sections of reheaters present potentially corrosive environments and medium and high alloys are recommended. This is especially important in applications involving bypass reheat where there may be excessive amounts of chlorine and sulfur trioxide. The tubes of direct reheaters should be high or medium alloy at the inlet and low alloy or carbon steel for the remaining tubes.

Damper selection is a complex matter and can itself provide the basis for a detailed study. The problems in damper selection are well known and need not be repeated here. The recommended materials of construction for the blades of inlet dampers are either carbon steel or low alloys. The blades of outlet dampers should be low alloys. Damper seals are continuously exposed to corrosive environments, and high alloys such as C-276 and 625 are recommended.

An FGD system is comprised of many subsystems, which when joined together, form a functioning unit. This paper has stressed the materials aspect of system design; it has avoided the chemical phenomena, the mechanical considerations and the other technologies that are incorporated into the design of a complete system. The point that must be stressed during the design of a system is that there is no best single material of construction for all components of all systems. There are many excellent products, made by established and reliable manufacturers. The choices are not always simple nor obvious. There are site specific situations that make selections that were optimal for one FGD system practically useless in another. In preparing this paper the authors have surveyed a broad spectrum of available materials and related these to the design, construction, and operation of several operating installations. They are intended to provide a place for the reader to begin investigation rather than a solution to all problems. Much progress has been made during the rather brief lifetime of the FGD industry. Much is continuously being learned, and much remains to be learned.

## ACKNOWLEDGEMENT

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# ACID DEPOSITION IN FGD DUCTWORK

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## BACKGROUND

In the mid 1970s, first generation wet lime/limestone flue gas desulfurization (FGD) systems were included in the design of many new coal-fired power plants across the United States in response to federal, state, and local sulfur dioxide ($SO_2$) emission control regulations. At the time, the primary concern within the electric power industry was whether the new systems would work at all. In retrospect, the overall performance of these FGD systems has been good. Based upon data from the best of these first generation systems, Congress and EPA have effectively mandated the use of FGD systems on all future coal-fired power plants. Continuous $SO_2$ reduction is the law of the land. Reliability is the new watchword for the utility industry.

For owners and operators of existing FGD systems and for designers and suppliers of new systems, problems with ductwork corrosion represent a major obstacle to the goal of 100 percent reliability. Corrosive failure of materials of construction in FGD system ductwork is a leading contributor to low reliability in existing FGD systems.

The corrosion experiences at the R. D. Morrow Station are a prime example of this industry-wide problem. The corrosion rates of the alloys and coating materials used at R. D. Morrow have been much higher than anticipated in the design. Some alloy materials chosen for repair of the initial corrosion on the basis of the results of laboratory corrosion tests in simulated FGD environments have also experienced rapid corrosion. In most cases, even coupon spool tests conducted at R. D. Morrow have been unable to predict the severe corrosion that has occurred when the test material was installed full-scale in the ductwork.

Based upon this experience it was concluded that: (1) the corrosive environment in the ductwork is more aggressive than that to which the spool coupons are exposed; and (2) the corrosive environment in the ductwork is more aggressive than that which had previously been simulated in the laboratory. It was clear that more and better data was needed to define the conditions that existed in the ductwork.

There was not sufficient information available regarding the chemical composition of the material that collects on the FGD ductwork surface. Collection, preservation and analysis of duct surface deposits obtained during periodic inspections at the time of system outages had proven to be difficult. Data from this type of sample was inconsistent and misleading. It became clear that there was a critical need for a method by which ductwork deposition samples could be obtained while the FGD system was operating.

Burns & McDonnell has identified and developed two innovative methods for characterization of the corrosive environment in FGD system ductwork. A predictive technique based on vapor-liquid equilibrium data for acid solutions is used to estimate acid concentrations in ductwork condensate. An extractive test method utilizing a controlled-temperature condenser is used for on-line collection of duct deposits from FGD system ductwork. Working under contract with EPRI (Research Project 1871-4), Burns & McDonnell conducted a test program at R. D. Morrow to evaluate the two methods. This paper describes these two methods and their applicability to the solution of corrosion problems in FGD system ductwork.

## OCCURRENCE OF ACID CONDENSATION IN FLUE GAS DUCTWORK

Flue gas from the combustion of coal contains a number of different acids in the form of condensable vapors. These acid vapors are present in trace concentrations in the gas stream. Sulfuric acid ($H_2SO_4$) is the most common, but hydrochloric acid (HCL), hydrofluoric acid (HF), hydrobromic acid (HBr) and nitric acid ($HNO_3$) may also be present.

If the temperature of the flue gas stream, or of the surfaces to which the gas stream is exposed, drops below the acid dew point temperature, acid condensate will form. The condensate may appear either as a thin film on the duct surfaces, or as aerosol droplets entrained in the gas stream, or a combination of the two. The acid dew point temperature for each of the condensable acid vapors listed above can be calculated from thermodynamic relationships. These relationships have been reduced to relatively simple equations that express the acid dew point temperature for each acid as a function of the acid vapor concentration and the water vapor concentration in the flue gas stream.

The relationship between $H_2SO_4$ vapor concentration and sulfuric acid dew point, at some constant $H_2O$ vapor content, is commonly displayed as the familiar "acid dew point curve." The family of dew point curves shown in Figure 1 illustrates the effect of flue gas moisture content on the sulfuric acid dew point.

Considering that $H_2SO_4$ vapor concentration in the flue gas from coal-fired boilers may be as much as 1 to 3 percent of the $SO_2$ concentration, it is apparent from Figure 1 that sulfuric acid condensate will form in ductwork downstream of the air heaters, where flue gas temperatures are typically less than 300 degrees F. For example, consider a flue gas containing 2,000 ppm

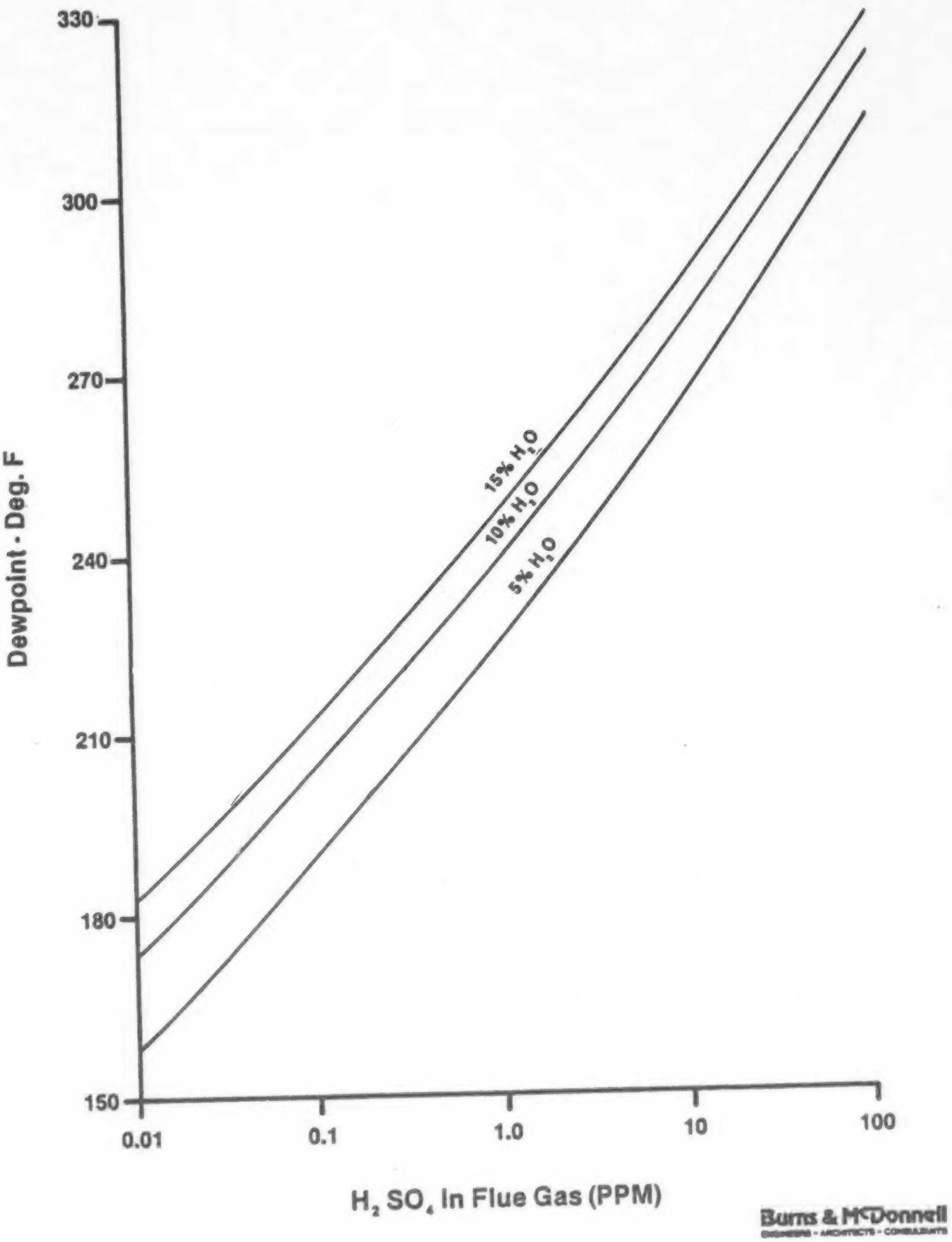


Figure 1. Effect of Flue Gas $H_2SO_4$ Vapor Concentration and Moisture Content on Acid Dewpoint

$SO_2$. At 1 percent conversion to $H_2SO_4$ this represents 20 ppm $H_2SO_4$ vapor in the flue gas. If the moisture content is 7.5 percent by volume, the sulfuric acid dew point temperature, from Figure 1, is approximately 285 degrees F.

When this flue gas enters a wet FGD system the temperature drops rapidly and the moisture content increases. The sudden drop to temperatures well below the acid dew point results in the condensation of most of the $H_2SO_4$ vapor as aerosol droplets (acid mist). This acid aerosol remains entrained in the gas stream. Due to the small diameter of the droplets a large percentage of the total mass of the $H_2SO_4$ can pass through the absorption system without being removed from the gas stream.

The high-moisture, low-temperature conditions of the absorber outlet gas stream are also conducive to the condensation of the other acid vapors, which typically have dew points much lower than that for sulfuric acid.

## CHARACTERIZATION OF FGD DUCTWORK ENVIRONMENT

Acid condensation in flue gas ductwork is common. Yet acknowledgement of this fact does not explain why severe corrosion has occurred at one FGD installation and not another, or why corrosion rates observed in full scale installations have been often much greater than those predicted from laboratory corrosion tests. As an important step toward the answer to these questions, two methods have been used to characterize the corrosive environment which exists in the ductwork of FGD systems. One method is a predictive technique based on empirical vapor-liquid equilibrium data for acid solutions. The second is an extractive test method which collects simulated duct surface deposits for chemical analysis.

### PREDICTIVE TECHNIQUE

The first method for characterization of acid condensate in FGD system ductwork involves the use of vapor-liquid equilibrium data for acid solutions as a function of temperature and acid solution concentration. As noted above, flue gas temperatures or duct surface temperatures below the acid dew point will result in formation of an acid condensate. The condensate will be a solution of the acid in water. The concentration of the acid solution that forms in this manner can be predicted from the analysis of vapor pressure data for the acid in question.

#### Physical Principle

The flue gas contains a certain percentage of water vapor, depending upon the moisture content of the coal, the ambient humidity, the amount of excess air and the flue gas saturation condition. The amount of water vapor in the flue gas varies from as little as six percent in the unscrubbed gas to 15 percent or more at the saturated conditions in the absorber and the absorber outlet ductwork.

In any case, the amount of water vapor in the flue gas is many times greater than the amount of acid vapor present. The total vapor pressure is therefore essentially a function of the moisture content only. When conditions are such that an acid condensate forms, the vapor above the condensate is in equilibrium with the liquid.

The equilibrium relationship between the composition of the vapor and the composition of the condensate is a function of temperature only. Consequently, if the temperature at which the condensate has formed is known, and if the moisture content of the vapor is known, the concentration of the acid in the condensate can be determined. Figure 2 displays this relationship in graphical form for the case involving sulfuric acid condensate.

## Examples

To illustrate the use of Figure 2, consider the same examples that were used previously. A flue gas with 7.5 percent moisture and 20 ppm $H_2SO_4$ (285 degrees F acid dew point) leaves the air heater at 300 degrees F. As this gas moves through the ductwork it encounters duct surface temperatures of 280 degrees F. A condensate film forms on the duct surface. From Figure 2, it is predicted that the condensate is between 80 and 85 percent $H_2SO_4$ by weight.

Now, the same flue gas passes through an electrostatic precipitator and into a wet limestone FGD system. The gas is cooled to the adiabatic saturation temperature of approximately 130 degrees F and humidified to 15 percent moisture by volume. The $H_2SO_4$ is condensed as an aerosol mist entrained in the flue gas. From Figure 2, the concentration of the acid in the aerosol droplets is about 10 percent $H_2SO_4$ by weight. Any remaining $H_2SO_4$ vapor that condenses on the surfaces of the outlet ductwork will also form condensate that is 10 percent or less $H_2SO_4$ by weight.

This type of graphical analysis using Figure 2 can be used for any case in which acid vapor and acid condensate are both present and equilibrium has been established. The data used to draw the curves of Figure 2 are derived from experimental measurements of vapor pressures over acid solutions of various concentrations over a wide range of temperatures. However, calculation of the data from thermodynamic relationships is also possible.

## Implications for FGD System Design

There are several important trends evident in the curves of Figure 2. It will be noted that acid condensate concentration is lowest when moisture content is high. Also, condensate concentration decreases with temperature. These phenomena are relevant to the design of FGD systems.

For example, consider the implication of the use of reheat. Flue gas reheat is accomplished by several methods. One method involves the bypass of an unscrubbed gas stream around the absorber for mixing with the scrubbed gas in the outlet ductwork or in the stack. The result is a gas which is warmer and dryer than the saturated gas leaving the absorber. From Figure 2 we see that both these characteristics will tend to increase the acid concentration in the aerosol droplets and/or the ductwork surface condensate film.

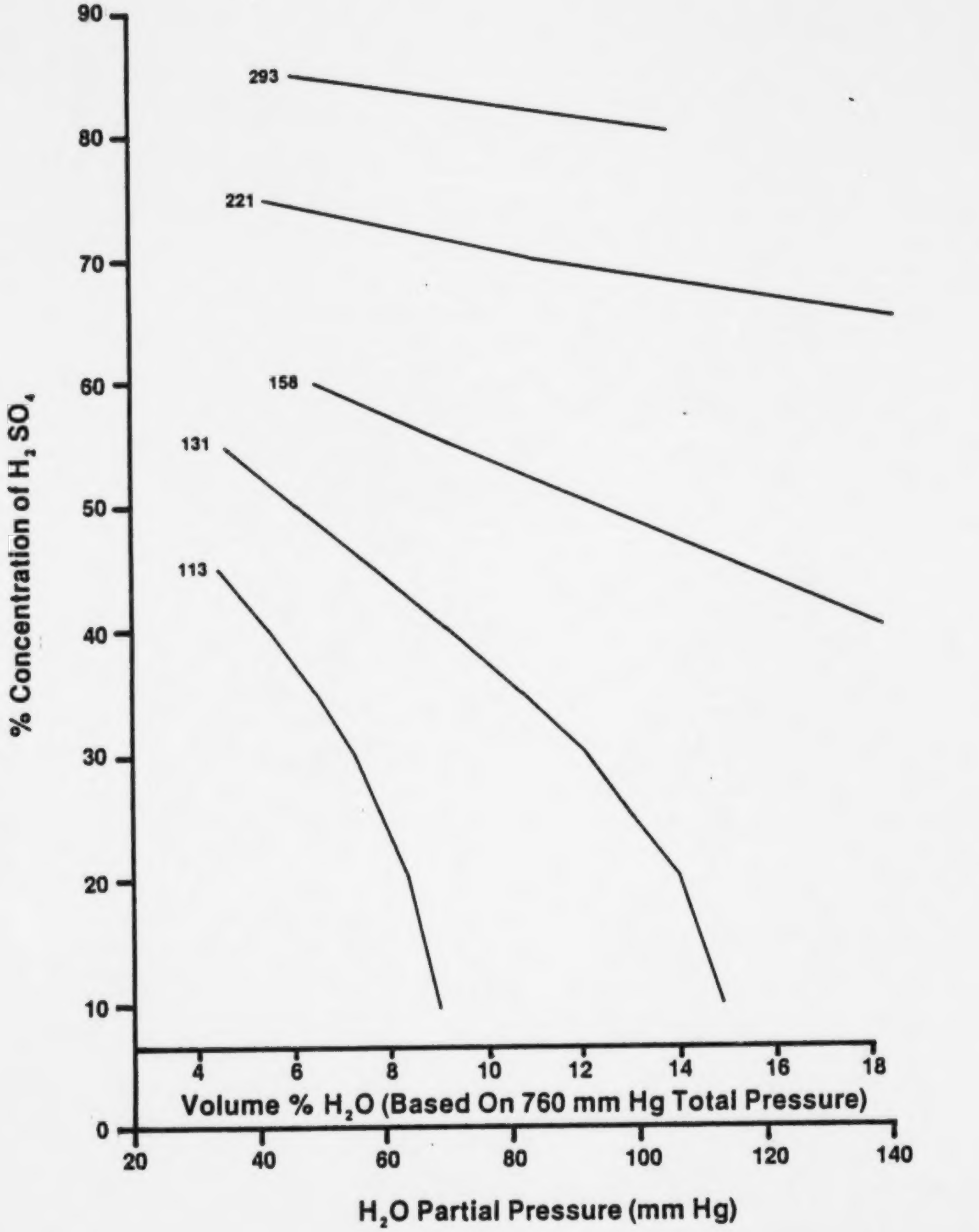


Figure 2. Effect of Flue Gas Moisture Content and Temperature on $H_2SO_4$ Concentration in Condensate

Another reheat method increases the temperature of the scrubbed gas without changing the moisture content. The effect of this type of reheat system is easily displayed on Figure 2. Consider the example case in which 15 percent moisture and 130 degrees F at the absorber outlet result in acid condensate that is 10 percent $H_2SO_4$ by weight. If a reheat system is used to provide a 30 degree F increase in flue gas temperature, the acid concentration in the aerosol droplets and/or the ductwork condensate film will increase to nearly 50 percent $H_2SO_4$ by weight. On this basis it is easy to understand why corrosion of reheater tubes is such a common problem.

## SELECTIVE ACID DEPOSITION TEST METHOD

The second method for characterization of the FGD ductwork environment is a flue gas testing procedure that Burns & McDonnell calls the Selective Acid Deposition (SAD) Test Method. This test procedure is designed to provide positive information on the composition of the material deposited on the surfaces of ductwork during operation of FGD systems. Although it is much more complex and difficult to use than the predictive technique method it has several significant advantages over that method.

- SAD testing can identify the effects of fly ash on the composition of the duct surface deposits. (The predictive technique is based on data from pure two-component mixtures of acid and water under laboratory conditions.)

- SAD testing can detect the presence of an acid condensate that was not known or expected to occur in the duct deposit. (The predictive technique method requires an assumption that the acid in question is present and that the temperature under consideration is below the dew point for that acid.)

- SAD testing can provide a complete analysis of the chemical composition of the duct surface deposit. (The predictive technique is limited to use for those acid solutions for which laboratory vapor pressure data are available.)

### Physical Principle

FGD system ductwork deposits can form by a number of different mechanisms. Acids, most commonly sulfuric acid, can condense from the flue gas onto the duct surface. Particulate can adhere directly to the duct surface or be trapped by the acid condensate film. Gas molecules and liquid aerosol droplets can be adsorbed onto the duct surface or onto the surfaces of the particulate that collects there. Gases may also be absorbed into the condensate film. The SAD sampling apparatus is designed so that all of these deposition mechanisms can occur in the sampling train just as they do in the ductwork.

In an operating FGD system, the interior surface of the ductwork is not at the same temperature as the flue gas stream. Temperature gradients result from convective and radiative heat transfer from the gas to the duct wall, through the insulation (if any), and ultimately to the outside air. The interior surface of the duct thus may be considerably cooler than the flue gas. Additional "cold spots" result from conductive heat transfer at locations where structural support members penetrate the insulation.

By allowing simulation of these heat transfer phenomena the SAD test method avoids one of the primary faults of the spool rack coupon corrosion test method. Because the coupons on a spool rack are thermally isolated from the duct surface, they are effectively maintained at the same temperature as the gas stream. This inability of the spool rack to simulate the actual conditions at the duct wall is believed to be the major cause of the discrepancy between performance of test materials and duct construction materials at R. D. Morrow with respect to corrosion resistance.

### Description of Test Method

The sampling train used for SAD flue gas testing is displayed in Figure 3. The sample is extracted isokinetically from the gas stream using a probe with a nozzle of appropriate diameter. Simulated duct deposits are collected by condensation and other mechanisms in the condensate trap. The thermostatically controlled oil bath maintains the condensate trap at the desired temperature. The impinger train is used to cool and dry the sample gas stream to protect the vacuum pump and the control module, which provides monitoring of sampling flows, pressures and temperatures.

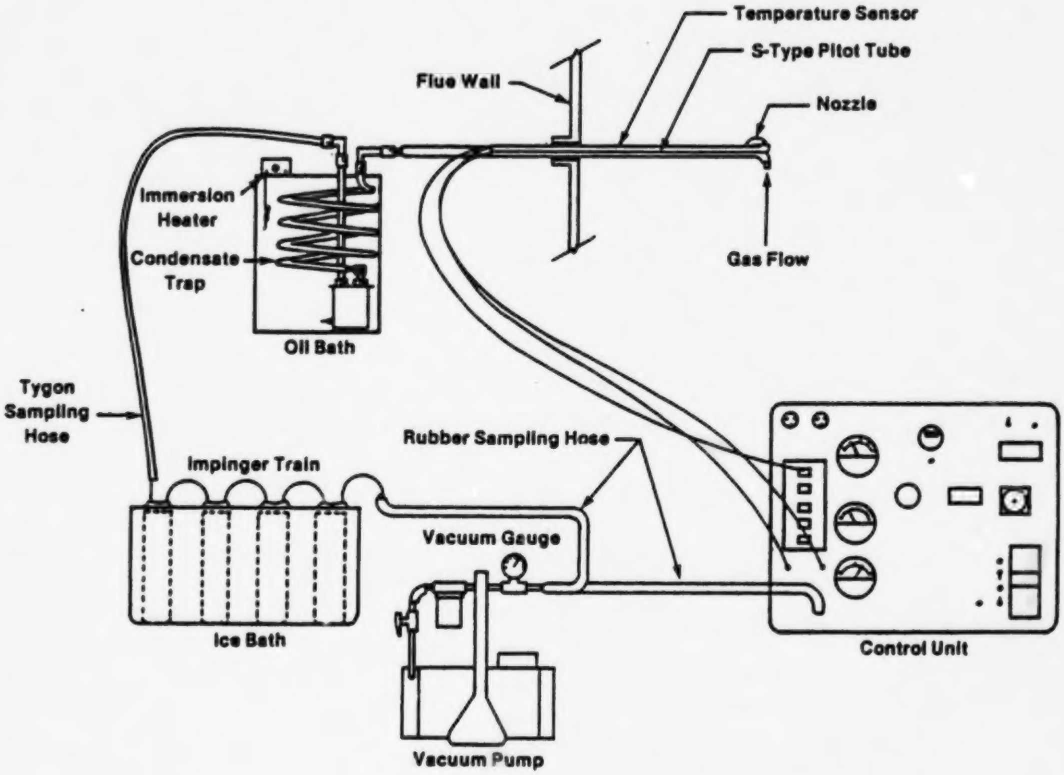
After collection, samples are recovered from the condensate trap by washing with deionized water. The samples are tested for a total of 37 chemical species by ion chromatography, inductively coupled argon plasma emission spectroscopy, and pH electrode. Constituent concentrations are reduced to terms of weight percent on a dry basis for comparison and analysis.

## SAD TESTING AT R. D. MORROW

### TEST PROGRAM

To provide an evaluation of the SAD test method for characterization of FGD ductwork acid deposition, two separate test programs were conducted at the R. D. Morrow Station during 1982. These test programs were conducted as part of EPRI Research Project RP 1871-4. The objective of the test programs also included investigation of the effects of FGD system operating conditions and duct surface temperatures on the composition of the ductwork deposits.

FGD system bypass (as a percentage of total gas flow) was varied from zero percent (full scrubbing) to 100 percent (full bypass) in increments of 20 percent. Simulated duct surface temperatures were varied from 20 degrees F below the flue gas temperature in the outlet ductwork mixing zone to as low as 100 degrees F. Test conditions are summarized in Table 1.



Burns & McDonnell
ENGINEERS - ARCHITECTS - CONSULTANTS

Figure 3. Sampling Train for SAD Test Method

## TABLE 1. SAD TEST CONDITIONS AT R. D. MORROW

| Percentage of Flue Gas Scrubbed | Mixing Zone Gas Temp. ($^oF$) | Condensate Trap Temperatures ($^oF$) |
|---|---|---|
| 100 | 130* | 130, 120, 100 |
| 80 | 160 | 140, 120, 100 |
| 60 | 200-240 | 220, 200, 180, 160, 140, 120, 100 |
| 40 | 245 | 225, 205, 185, 165 |
| 20 | 280 | 260, 240, 220, 200 |
| 0 | 300-320 | 300, 280, 260, 240, 220, 180, 140, 100 |

*Samples collected at absorber outlet. All other samples collected in stack.

Simulated duct surface temperatures in the range from 20 degrees F to 60 degrees F below the flue gas temperature represent conditions that could occur during steady-state FGD system operation, depending upon the gas temperature, the ambient temperature, and the thickness and condition of the ductwork insulation. The other duct surface temperatures simulated represent transient conditions that could occur only during start-up.

## TEST RESULTS

The SAD testing programs at R. D. Morrow generally confirmed that the test method can produce repeatable results with a reasonable degree of accuracy. The test method succeeded in collecting and identifying the constituents of the material deposited on a simulated duct surface during FGD system operation.

Simulated duct deposit samples from the R. D. Morrow FGD system were found to consist primarily of six constituents (Table 2).

## TABLE 2. SAD TESTING AT R. D. MORROW - SAMPLE COMPOSITION

| | Weight Percent in Sample (Dry Basis) | | | | | |
|---|---|---|---|---|---|---|
| Sample Constituent | Test 1 | | Test 2 | | All Samples | |
| | Mean | S.D.* | Mean | S.D. | Mean | S.D. |
| | (N=19) | | (N=15) | | (N=34) | |
| Sulfate | 62.2 | 25.0 | 54.6 | 19.6 | 58.9 | 22.7 |
| Chloride | 13.5 | 22.1 | 13.6 | 21.7 | 13.5 | 21.6 |
| Fluoride | 2.50 | 3.20 | 2.85 | 3.77 | 2.65 | 3.41 |
| Aluminum | 6.10 | 2.97 | 10.9 | 4.02 | 8.23 | 4.20 |
| Iron | 4.41 | 3.18 | 4.64 | 2.46 | 4.51 | 2.84 |
| Silicon | 1.44 | 1.10 | 3.90 | 2.26 | 2.53 | 2.09 |
| | 90.2 | | 90.5 | | 90.3 | |

*Standard Deviation.

The data presented in Table 2 support the following conclusions regarding the composition of the duct surface deposits.

- Sulfate is the dominant constituent of the deposits. Based upon its predominance compared to the metallic constituents it is clear that the primary source of the sulfate in the samples is sulfuric acid.
- The chloride and fluoride contents of the duct surface deposits are highly variable. (Reasons for this variability are addressed later.)
- The ash contents of the duct deposit samples from Test 2 are significantly higher than those from Test 1. This result can be explained from stack opacity levels, which were consistently much higher during Test 2 than during Test 1.

Other sample constituents observed frequently at levels of 1.0 percent or greater by weight are potassium, calcium, phosphorous, sodium, selenium and magnesium.

## Effects of Mixing Scrubbed and Unscrubbed Flue Gas

The R. D. Morrow FGD systems were designed for partial bypass of the flue gas around the absorber. This design reduced the size of the absorber required and provided for reheat of the scrubbed gas. The mixing of scrubbed and unscrubbed flue gas in the outlet ductwork had been suspected as one cause of the severe corrosion of the ductwork construction materials in this zone.

SAD test results from R. D. Morrow confirm that mixing of scrubbed and unscrubbed flue gas has a dramatic effect on duct surface deposit characteristics (Table 3).

TABLE 3. EFFECT OF MIXED GAS RATIO

| Mixed Gas Ratio Scrubbed/Unscrubbed | Sample Constituent | Weight Percent in Sample Dry Basis |
|---|---|---|
| 100/0 | Chloride | 5.70 |
| | Fluoride | 0.26 |
| 80/20 | Chloride | 66.0 |
| | Fluoride | 5.43 |

Based upon these test results it can be concluded that:

- Absorber removal efficiencies for HCl and HF are very high, possibly 98 percent or above.
- Even very small portions of bypassed gas mixed with scrubbed gas can result in order-of-magnitude increases in the halide content of the duct deposits. This could explain the occurrence of severe pitting corrosion of alloy materials in the mixing zone of the R. D. Morrow FGD outlet ductwork.

## Effect of Condenser Temperature

Analysis of vapor-liquid equilibrium data for sulfuric acid solutions indicates that variations in the SAD condensate trap temperature should produce corresponding changes in the concentration of $H_2SO_4$ in the condensate. However, the SAD test method as used at R. D. Morrow cannot detect changes in acid condensate concentration.

The condensate forms as a thin film on the surface of the condenser tubing. It was not possible at R. D. Morrow, in most cases, to determine the mass or volume of the condensate. Samples were recovered by washing the condenser with deionized water. Because the resultant constituent concentrations could not be related to "as condensed" acid solution concentrations, all data was reduced to a dry basis for analysis. Thus, for example, it was not possible to differentiate between a sample that condensed as a 50 percent $H_2SO_4$ solution and one that condensed as a 75 percent $H_2SO_4$ solution.

Despite this limitation, SAD test results from R. D. Morrow did provide information on the effects of condenser temperature on sample composition. Chloride and fluoride compositions of the samples were found to be a strong function of condenser temperature. Chloride composition of the samples was observed to increase sharply below 140 degrees F. Fluoride composition followed a similar, although more moderate, trend at temperatures below 165 degrees F. The data supporting these conclusions are summarized in Table 4. Da a for the full scrubbing case have been excluded from this analysis to isolate the temperature effect.

TABLE 4. EFFECT OF SIMULATED DUCT SURFACE TEMPERATURE

| Sample Constituent | Temperature Range ($^oF$) | Weight Percent in Sample Dry Basis |
|---|---|---|
| Chloride | Less than 140 | 51.6 |
| | 140 and above | 3.41 |
| Fluoride | Less than 165 | 6.38 |
| | 165 and above | 0.532 |

The fact that both chloride and fluoride exhibit such a marked dependence on condenser temperature indicates that the primary source of each constituent is a vapor that condenses in the sampling train. The occurrence of nonzero values for the compositions of these constituents at the higher temperatures reflects the fact that they also exist in the flue gas in solid form as components of the fly ash.

## CONCLUSIONS AND RECOMMENDATIONS

Two methods for characterization of the corrosive environment in FGD system ductwork have been developed by Burns & McDonnell. Each method can provide important information on the composition of the acidic material that collects on duct surfaces by condensation and other mechanisms.

The predictive technique can be used in the planning and design of new FGD systems to identify the concentrations of acid solutions that will condense on ductwork surfaces. This information should be used to evaluate the acceptability of alternative corrosion-resistant materials for duct construction and/or lining.

For operating FGD systems that are experiencing corrosion problems in ductwork, the SAD test method can be used to provide complete chemical characterization of the material that is deposited on the duct surfaces during operation. The test results should be used to define the corrosive environment to which ductwork construction materials and/or linings are being exposed. This environment can then be duplicated in laboratory corrosion tests to identify the proper corrosion-resistant material required for solution of the problem.

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# IN SITU EVALUATION OF HIGH PERFORMANCE ALLOYS IN POWER PLANT FLUE GAS DESULFURIZATION SCRUBBERS

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## ABSTRACT

Preliminary data from ongoing in situ FGD scrubber exposure tests, involving specific high performance stainless steels, nickel-base and titanium alloys are presented and discussed. Spool rack exposures of 4-9 month duration involving candidate alloys, Titanium Grades 2 and 12, 904L stainless steel and nickel-base Alloys 625 and C-276, were conducted in the inlet quench and outlet duct zones of several operating power plant FGD scrubber systems. In general, the titanium alloys exhibited performance equal to or superior to the steel and nickel alloys, particularly in outlet ducts. The 904L alloy consistently exhibited poor resistance to localized attack, while 625 and C-276 alloy performance was varied. These findings are discussed relative to specific environmental considerations, and parallel laboratory and field studies reported in the literature.

## INTRODUCTION

The flue gas desulfurization (FGD) scrubber industry is in a state of flux, not only in terms of changes in process technology, but also relative to the materials of construction used in the systems. In the early 1970's when the FGD industry was beginning, carbon steel and low alloy austenitic stainless steels were used as materials of construction in what was considered to be a mild environment. As time progressed, these materials were found to be unsatisfactory, and highly alloyed austenitic stainless steels and some nickel-base alloys became the accepted construction materials. However, these alloys still have their limits, and some FGD systems have experienced such severe corrosion in recent years that more corrosion resistant alloys are now being considered(1) to limit costly downtime and maintenance.

FGD scrubber systems are composed of a variety of equipment(2) from prescrubbers and absorber vessels to dampers, ducts, stacks, and piping systems. However, the major material problem areas are the wet/dry interfaces at the inlet quench (pre-scrubber) and the mixing/reheat zone.(3) Additionally, the entire outlet duct, from the mist eliminators to the stack, can be subjected to severely corrosive conditions of low pH, high chloride levels, and relatively high (or fluctuating) temperatures. Outlet duct problems are also associated with acidic gases near or below the dew point. The test program reported on in this paper is concentrated in these areas.

Several laboratory and in situ programs(4-13,19,22,23) for evaluating resistant scrubber materials, in addition to actual service experience,(14-18) have been reported in the literature. Limitations in performance of highly alloyed stainless steel and nickel alloys are noted, particularly in closed-loop systems. Laboratory studies suggest that acidic chlorides, in conjunction with possible fluoride interactions,(18,19) are primarily responsible for limitations in pitting and crevice corrosion resistance of the high performance alloys evaluated to date.

The relatively few evaluations conducted in the past to identify severe inlet and outlet duct corrosion problems have not included all candidate metals and alloys (e.g. Alloys 904L, 625, C-276, and Titanium Grades 2 and 12), or have involved conditions not directly representative of actual scrubber environments. In particular, titanium alloys, noted for their resistance to hot chloride environments, have been evaluated only to a very limited extent.

Early in situ tests in an FGD scrubber and a copper smelting limestone scrubber(20) indicated that unalloyed titanium, C-276 and 625 alloys, were the most resistant materials, exhibiting no measurable attack. Similar results were reported in several municipal refuse incinerator flue gas scrubbers(21) and for simulated outlet duct exposures.(22) Recent laboratory studies, in fact, suggest that titanium's potential suitability in FGD scrubber environments may be due to inhibiting effects of flyash.(23)

The major factor limiting consideration of titanium and other resistant alloys has been material cost. Table 1 summarizes relative material costs, normalized per unit surface area, of candidate corrosion-resistant alloys for problem areas in FGD scrubbers. Clearly, titanium represents a cost-effective alternative to highly alloyed ferrous and nickel alloys and, thus, should be considered as an alternate material of construction.

The spool rack test program discussed in this report was performed to provide a comprehensive in situ evaluation of the corrosion resistance of potentially viable high-performance alloys, including titanium. Because the alloys were tested in the same FGD scrubber locations, direct comparison of their corrosion resistance is possible, allowing for possible ranking of materials. Additionally, the range of alloys and the variety of environments tested should allow for a more complete comparison with previous in situ scrubber experience and laboratory

TABLE 1. COST COMPARISONS (PER UNIT SURFACE AREA)
OF CANDIDATE ALLOYS FOR CORROSIVE FGD SCRUBBER SERVICE

| Alloy | Density (lb/cu in) | Weight (lb/sq ft) | Relative Alloy Cost* (Per Unit Surface Area) | Relative Total Cost** Including Fabrication (Per Unit Surface Area) |
|---|---|---|---|---|
| 904L | 0.289 | 10.5 | 0.52 | 0.60 |
| 825 | 0.294 | 10.6 | 0.99 | 0.94 |
| Ti-Grade 2 | 0.163 | 5.9 | 1.00 | 1.00 |
| Ti-Grade 12 | 0.163 | 5.9 | 1.20 | 1.13 |
| G | 0.300 | 10.8 | 1.23 | 1.09 |
| 625 | 0.305 | 11.0 | 1.86 | 1.52 |
| Ti-Grade 7 | 0.163 | 5.9 | 1.89 | 1.63 |
| C-276 | 0.321 | 11.6 | 2.11 | 1.69 |

*Based on mill quantity quotes for 6.35-mm plate product as of May 1983.

**Assumes a 2:1 contribution of material to fabrication cost for overall cost.

results.

## EXPERIMENTAL

### ALLOYS EXPOSED

High-performance alloys evaluated in this investigation included C.P. Grade 2 titanium, Grade 12 titanium (Ti-Code 12), Alloy C-276, Alloy 625, and Alloy 904L. Stainless steel 20Cb-3 and 316L were also evaluated in one scrubber. Nominal compositions of these alloys are presented in Table 2. The Grade 2 titanium represents common unalloyed titanium, whereas Grade 12 titanium includes alloy additions of 0.3% Mo and 0.8% Ni, which provide improved crevice corrosion resistance compared to unalloyed titanium grades. Alloys C-276 and 625 are highly alloyed nickel alloys containing molybdenum contents of 16 and 9 weight percent, respectively, that possess relatively good resistance to localized chloride attack. The 904L and 20Cb-3 alloys are super-austenitic stainless steels.

All alloys were tested as 3.18-mm (0.125-in) sheet product in the mill-annealed condition.

### SPECIMEN PREPARATION/EVALUATION

Specimens consisted of 50.8-mm (2-in) square 3.18-mm (0.125-in) sheet, containing a 7.9-mm (.31-in) diameter center hole for mounting. The two titanium alloy specimens were prepared by a light pickle in 35 vol % $HNO_3$-5 vol % HF solution, rinsing in distilled water, and drying before weighing. The nickel and stainless steel alloys were abraded dry with 120 grit alumina paper, followed by a distilled water rinse. Specimen weights were measured to one-tenth of a milligram.

Weldments of each alloy were prepared by standard (argon-shielded) autogenous TIG weld procedures. For each welded specimen, one weld pass was performed on a single specimen face, with full specimen thickness penetration.

Corrosion coupons were mounted onto an unalloyed titanium spool rack, such that three specimens of each titanium alloy and two specimens of each of the C-276, 625, and 904L alloys were included. One coupon of each alloy consisted of a welded specimen. Figure 1 illustrates a fully assembled spool rack ready for exposure.

Flat Teflon® washers, 9.53-mm (.375-in) thick, provided coupon separation in addition to a 14.8-$mm^2$ (0.23-$in^2$) effective crevice surface area on every coupon face. Teflon® insulating sleeves were used to prevent spool rack or intercoupon galvanic interactions.

Post-exposure evaluation included specimen weighing, microscopic examination at 10-30x, and maximum pit depth measurement after thorough specimen cleaning. Removal of tenacious solid surface deposits was difficult via conventional inhibited-acid cleaning techniques.

TABLE 2. NOMINAL COMPOSITIONS OF HIGH PERFORMANCE ALLOYS EVALUATED IN IN SITU SCRUBBER EXPOSURES

| Alloy | Weight % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Ti | Ni | Fe | Cr | Mo | W | Cu | C | Others |
| Grade 2 Titanium | Bal | — | 0.12 | — | — | — | — | .02 | .01N, 0.12$O_2$ |
| Grade 12 Titanium | Bal | 0.80 | 0.12 | — | 0.30 | — | — | .02 | .01N, 0.12$O_2$ |
| Alloy C-276 | — | Bal | 5.0 | 16.0 | 16.0 | 4.0 | — | .01 | 0.3V |
| Alloy 625 | — | Bal | 2.5 | 21.5 | 9.0 | — | — | .05 | 3.5 Cb + Ta |
| Alloy 904L | — | 25.0 | Bal | 19.5 | 4.5 | — | 1.5 | .02 | — |
| Alloy 20Cb-3 | — | 34.0 | Bal | 20.0 | 2.5 | — | 3.5 | .02 | 1Mn, .5Cb, .5Si |
| Alloy 316L | — | 12.0 | Bal | 17.0 | 2.0 | — | — | .03 | 2Mn, 1Si |

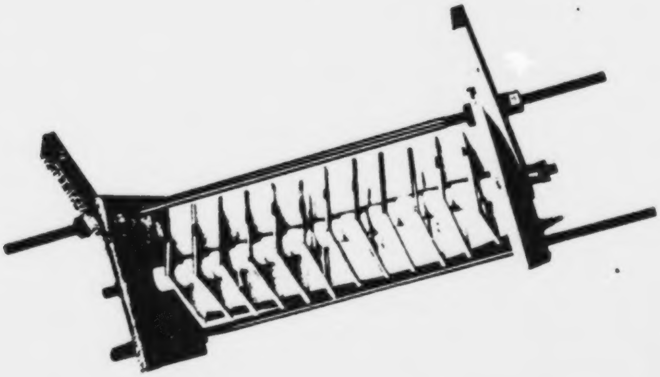

Figure 1. Fully assembled corrosion test spool rack for in situ scrubber exposure evaluation of alloys.

Specimen cleaning utilizing a brass wire brush and a warm detergent solution proved successful in this regard. Pit depths were measured to the nearest 0.025-mm (0.001-in), using a depth-measuring microscope by focusing on the edge and bottom of each pit.

## IN SITU SCRUBBER EXPOSURE SITES

Spool racks were installed in FGD scrubbers of the following four power plants with the cooperation of power plant personnel: South Mississippi Electric Power - R.D. Morrow Sr. Power Plant, Indianapolis Power and Light - Petersburg Station, Allegheny Power Service Corporation - Pleasants Station, and Potomac Electric Power - Dickerson Station. FGD scrubbers associated with the first three power plants are limestone slurry absorption systems for flue gas $SO_2$ removal. The R. D. Morrow scrubber represents the only closed-loop system evaluated, generally providing the most aggressive conditions, resulting from high chloride and fluoride levels in the recycled slurry. Outlet duct gas reheat is achieved with bypassed flue gas for all three limestone scrubber systems.

The PEPCO-Dickerson Station utilizes a variable-throat venturi particulate scrubber for direct flyash removal and partial $SO_2$ absorption. The scrubbing media is partially recycled water, resulting in low media pH's relative to the buffered limestone slurry systems.

The most corrosive areas of the inlet and outlet scrubber ducting, based on previous individual scrubber experience, were chosen for spool rack exposure. In this regard, the inlet quench duct (wet/dry gas interface zone), mixing zone, and breech duct were selected at the R. D. Morrow Sr. Plant. At the Petersburg Station, the presaturator (water spray quench) and mixing zones provided potentially aggressive environments for evaluation. Spool racks were attached to a duct expansion joint shield between the mixing and breech duct zones at the Pleasants Station. Among the most aggressive areas of the Dickerson Station's particulate scrubber was the vapor zone at the base of the stack (above the sump). Conditions associated with each of these specific exposure sites are outlined in Table 3.

A pair of (identical) spool racks were installed in each designated scrubber location. This allowed four to seven month, and eight to twelve month exposure data to be collected. With the exception of R. D. Morrow Sr. Plant exposures, to date, only four to seven month data has been obtained for discussion in this report.

## RESULTS OF IN SITU SCRUBBER EXPOSURES

### R. D. MORROW SR. PLANT CORROSION DATA

Corrosion data generated from R. D. Morrow's Scrubber No. 1 mixing zone after five and nine-month exposures are presented in Table 4. Weight loss values clearly indicate no measurable corrosion on Titanium Grades 2 and 12, whereas significant attack is evident for Alloys 625,

TABLE 3. EXPOSURE CONDITIONS FOR INDIVIDUAL SCRUBBER DUCT ZONES EVALUATED

| Power Plant | Scrubber Zone | Temp (°C) | Chlorides (ppm) | pH | Other Factors |
|---|---|---|---|---|---|
| R. D. Morrow Sr. Plant | Inlet quench duct (Scrubber #1) | 52-177 | >15,000 | 1.0-5.4 | Wet/dry gas interface zone |
| | Mixing Zone (Scrubber #1) | 52-177 | 3,100-10,000 | 1.3-2.4 | " " " " |
| | Breech Duct (Scrubber #1) | 106-115 | 3,000-10,000 | 1 - 3 | -- -- |
| Petersburg Station | Inlet Presaturator (D-Module) | 54-149 | > 3,000 | 1.0-3.5 | Water spray quench |
| | Mixing Zone (3-2 Scrubber) | 66-149 | — | — | Wet gas 70% of exposure |
| Pleasants Station | Mixing/Breech Duct Zone | 52-149 | — | — | — — |
| Dickerson Station | Base of Stack | 82 | 1,270 | 1.6-2.2 | Wet gas above stack sump |

TABLE 4. R. D. MORROW SR. POWER PLANT FGD SCRUBBER NO. 1 - MIXING ZONE CORROSION DATA

| Alloy Exposed | Specimen Type | Weight Loss (Δ mg) | | | Max Pit Depth* (Mils) | |
|---|---|---|---|---|---|---|
| | | 5 Mo. | (9Mo.) | Avg | 5 Mo. | (9 Mo.) |
| Grade 2 Titanium | Base | Nil | ( Nil) | Nil (Nil) | 0, 0 | (0, 0) |
| | Base | Nil | ( Nil) | -- | 0, 0 | (0, 0) |
| | Welded | Nil | ( Nil) | | 0, 0 | (0, 0) |
| Grade 12 Titanium | Base | Nil | ( Nil) | Nil (Nil) | 0, 0 | (0, 0) |
| | Base | Nil | ( Nil) | -- | 0, 0 | (0, 0) |
| | Welded | Nil | ( Nil) | | 0, 0 | (0, 0) |
| Alloy C-276 | Base | 32 | ( 76) | -- | 4, 2 | (16**, 0) |
| | Welded | 61 | ( 86) | -- | 19**,5**,3 | (35**, 0) |
| Alloy 625 | Base | 186 | ( 374) | -- | 1,3**,1 | (70,4**) |
| | Welded | 357 | ( 557) | -- | 29,21 | (38**,43**,1) |
| Alloy 904L | Base | 1724 | (2708) | -- | Perforated | (Perforated) |
| | Welded | 1940 | (2844) | -- | 54,93 | (Perforated) |

*Maximum pit depth data given for both specimen faces.
**Pit formed in Teflon®-metal crevice.

C-276, and 904L. The extent of attack on the nickel and 904L alloys appears to increase non-linearly with exposure period.

Correspondingly, the pit depth data reveals no localized attack on any titanium coupons (Figures 2 and 3), with severe pitting occurring on Alloys C-276, 625 and 904L specimens. In fact, Alloy 904L samples exhibited extensive perforation from pitting, in addition to shallow surface craters resulting from deposit crevice corrosion (Figure 4). The majority of the weight loss observed on C-276 specimens is attributable to Teflon®-metal crevice corrosion. Crevice attack on the two nickel alloys generated pit depths as large as 30-40 mils (Figures 5 and 6). The 625 alloy also displayed 20-30 mil pits of small diameter-to-depth ratios, independent of Teflon®-to-metal crevices.

Breech duct corrosion data is outlined in Table 5. Again, titanium alloys experienced near nil corrosion, demonstrated by very low weight loss and no pitting. The C-276 alloy coupons similarly displayed insignificant weight loss, but did indicate incipient pitting and Teflon®-metal crevice attack, penetrating 1-3 mils deep. The 904L and 625 alloys revealed pit depths of up to 8 mils, with associated increases in net weight loss. Incipient crevice attack of Alloy 625 in Teflon®-metal crevices was also noted.

Compared to the mixing zone, the breech duct proved to be significantly less aggressive to nickel and stainless steel alloys. The trend in relative overall corrosion resistance, however, is consistent in both outlet duct exposures after five and nine months:

Titanium Grade 2, 12 > C-276 > 625 > 904L

None of the high-performance alloys exposed to the wet/dry gas zone of the inlet quench duct were immune to attack. Table 6 shows that, contrary to outlet duct performance, both Titanium Grades 2 and 12 displayed extensive localized attack considered to be deposit crevice corrosion (Figure 7). The C-276 and 625 alloys exhibited very shallow surface pits ranging in depths to 6 mils. Enlarged views of this attack are illustrated in Figures 8 and 9. In this zone, the nickel-base alloys proved to be more resistant to localized attack. Susceptibility to Teflon®-metal crevice attack for all alloys was somewhat diminished in this zone compared to the mixing zone.

## PETERSBURG STATION CORROSION DATA

At the Petersburg Station, both outlet and duct mixing zone and inlet presaturator environments were evaluated. The mixing zone (Table 7) proved to be very benign to all alloys tested including 316L, 904L, and 20Cb-3 stainless steels. This appears to reflect low chlorides in the scrubber outlet gas, and spool rack positioning relative to the mixing zone wet/dry gas interface.

Conditions in the water spray D-Module presaturator provided a more discriminating test of alloys (Table 8). After seven months,

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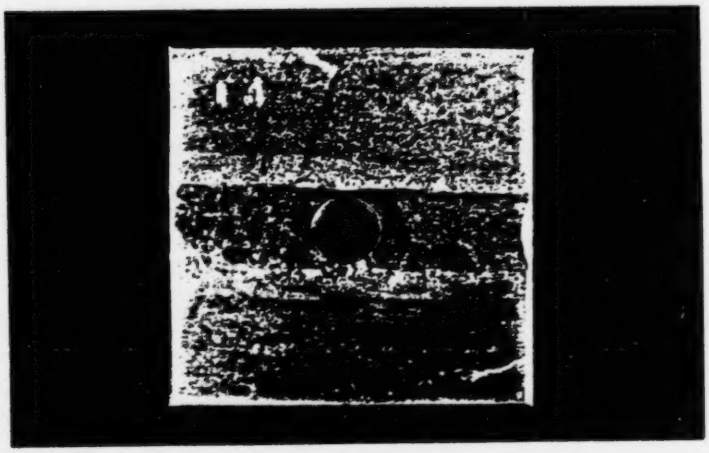

Figure 2. Grade 2 titanium welded coupon (as-cleaned) after 9-month exposure in the mixing zone of R. D. Morrow Sr. Scrubber No. 1.

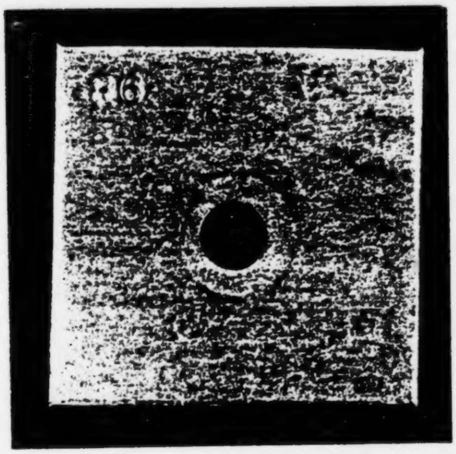

Figure 3. Grade 12 titanium base metal coupon (as-cleaned) after 9-month exposure in the mixing zone of R. D. Morrow Sr. Scrubber No. 1.

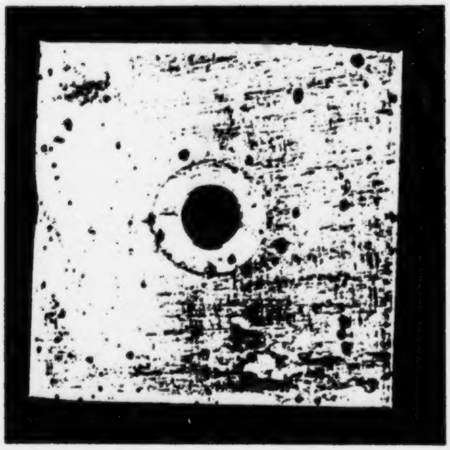

Figure 4. Alloy 904L base metal coupon (as-cleaned) after 9-month exposure in the mixing zone of R. D. Morrow Sr. Scrubber No. 1.

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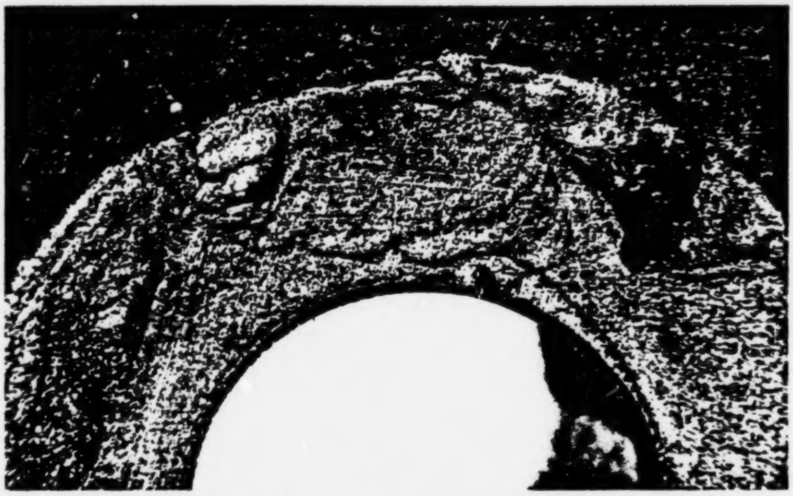

Figure 5. Crevice corrosion and pitting on Alloy 625 (at 8x) after 9-month exposure in the scrubber mixing zone at the R. D. Morrow Sr. Station.

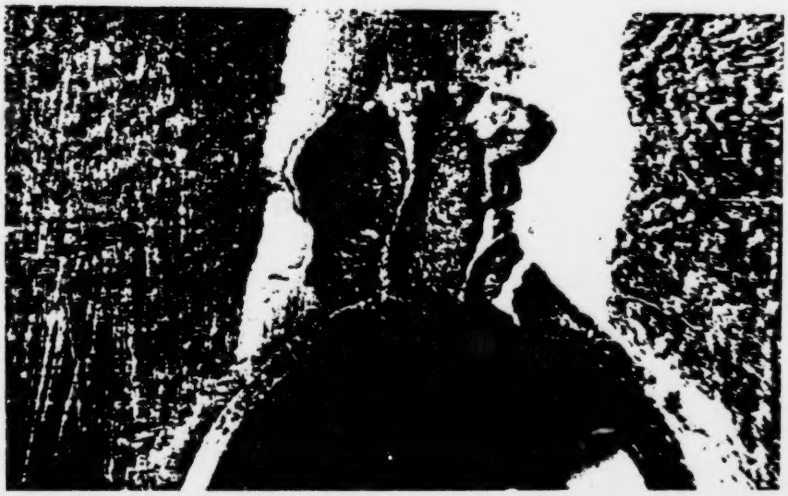

Figure 6. Crevice corrosion on Alloy C-276 weld coupon (at 8x) after 9-month exposure to the scrubber mixing zone at the R. D. Morrow Sr. Station.

## TABLE 5. R. D. MORROW SR. POWER PLANT
## FGD SCRUBBER NO. 1 - BREECH DUCT CORROSION DATA

| Alloy Exposed | Specimen Type | Weight Loss (Δ mg) | | | Max Pit Depth* (Mils) | |
|---|---|---|---|---|---|---|
| | | 5 Mo. | (9 Mo.) | Avg | 5 Mo. | (9 Mo.) |
| Grade 2 Titanium | Base | 4 | ( 18) | 4 (16) | 0, 0 | (0, <1) |
| | Base | 3 | ( 14) | | 0, 0 | (0, 0) |
| | Welded | 14 | ( 18) | -- | 0, 0 | (0, 0) |
| Grade 12 Titanium | Base | 5 | ( 14) | 3 (20) | 0, 0 | (0, <1) |
| | Base | 1 | ( 25) | | 0, 0 | (0, 0) |
| | Welded | 2 | ( 15) | -- | 0, 0 | (0, 0) |
| Alloy C-276 | Base | 12 | ( 27) | -- | 0, 2** | (0, 1**) |
| | Welded | 17 | ( 35) | | 0, 3 | (3, 2) |
| Alloy 625 | Base | 76 | ( 66) | -- | 1, 2 | (1**, 1**) |
| | Welded | 87 | ( 68) | | 5,2**,1 | (1**, 1**) |
| Alloy 904L | Base | 140 | (122) | -- | 5, 3 | (1, 2) |
| | Welded | 140 | (120) | | 8, 5 | (3, 2) |

*Maximum pit depth data given for both specimen faces.
**Pit formed in Teflon®-metal crevice.

## TABLE 6. R. D. MORROW SR. POWER PLANT
## FGD SCRUBBER NO. 1 - INLET QUENCH CORROSION DATA

| Alloy Exposed | Specimen Type | Weight Loss (Δ mg) | | | Max Pit Depth* (Mils) | |
|---|---|---|---|---|---|---|
| | | 5 Mo. | (9 Mo.) | Avg | 5 Mo. | (9 Mo.) |
| Grade 2 Titanium | Base | Nil | (479) | Nil (313) | 0, 0 | (11, 37) |
| | Base | Nil | (147) | | 0, 0 | ( 7, 9) |
| | Welded | Nil | (547) | -- | 0, 0 | (26, 26) |
| Grade 12 Titanium | Base | Nil | (319) | Nil (402) | 5, 0 | (10, 18) |
| | Base | Nil | (485) | | 0, 0 | (23, 19) |
| | Welded | Nil | (592) | -- | 0, 0 | (24, 18) |
| Alloy C-276 | Base | 38 | ( 69) | -- | 4, 2 | ( 1, 1) |
| | Welded | 42 | ( 82) | | 1, 3 | ( 6, 2) |
| Alloy 625 | Base | 51 | ( 99) | -- | 2, 1 | ( 1, 3) |
| | Welded | 49 | (106) | | 2, 2 | ( 2, 8) |
| Alloy 904L | Base | 92 | (216) | -- | 4, 8 | ( 4, 11) |
| | Welded | 95 | (265) | | 9, 5 | ( 6, 8) |

*Maximum pit depth data given for both specimen faces.

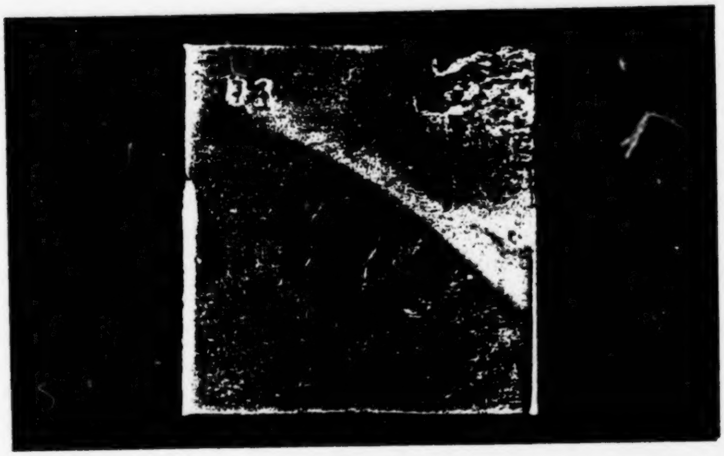

Figure 7. Localized attack on Grade 12 titanium base metal coupon after 9-month exposure to the wet/dry zone of the inlet quench duct at the R. D. Morrow Sr. Plant.

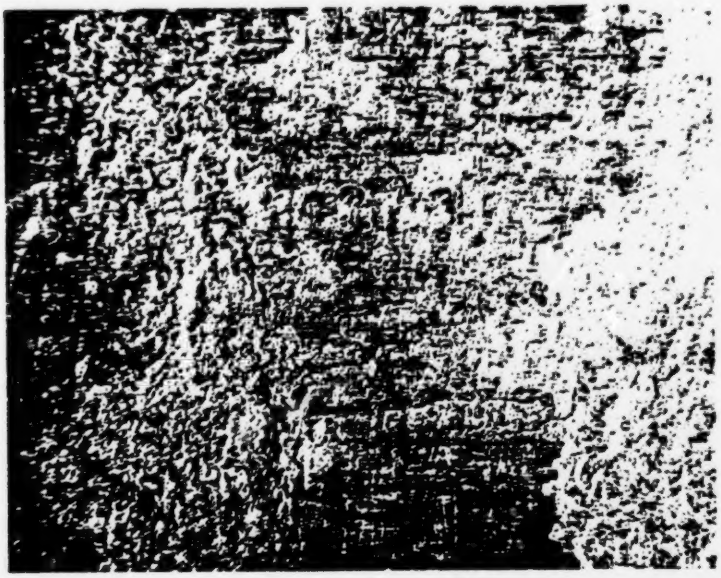

Figure 8. Shallow surface pitting of Alloy C-276 (at 8x) after 9-month exposure to the wet/dry zone of the inlet quench duct at the R. D. Morrow Sr. Plant.

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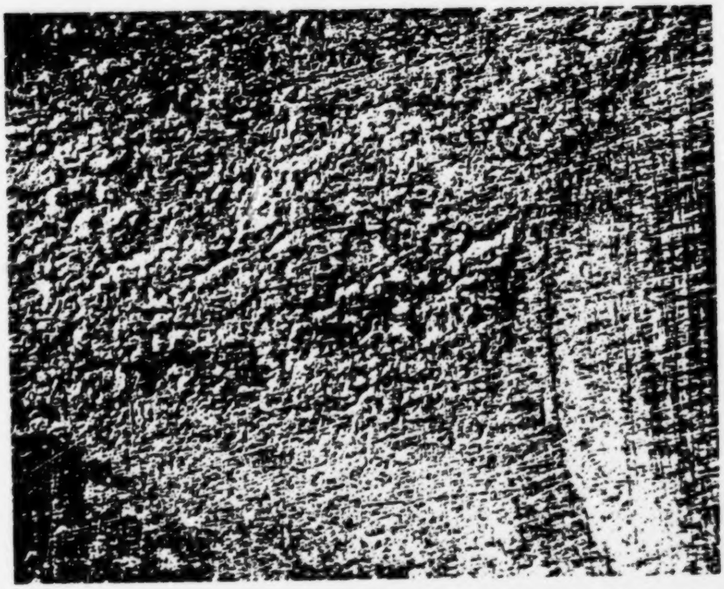

Figure 9. Shallow surface pitting of Alloy 625 (at 8x) after 9-month exposure to the wet/dry zone of inlet quench duct at the R. D. Morrow Sr. Plant.

## TABLE 7. PETERSBURG STATION CORROSION DATA

FGD Scrubber - 3/2 Outlet Mixing Zone
(4.5-Month Exposure)

| Alloy Exposed | Specimen Type | Weight Loss (mg) | Max Pit Depth* (mils) |
|---|---|---|---|
| Grade 2 Titanium | Base | 41 | 0, 1 |
| Grade 2 Titanium | Welded | 40 | 1, 1 |
| Grade 12 Titanium | Base | 135 | 0, 0 |
| Grade 12 Titanium | Welded | 143 | 1, 1 |
| Alloy 625 | Base | 170 | 1, 2 |
| Alloy 625 | Welded | 176 | 1, 1 |
| Alloy 904L | Base | 31 | 0, 0 |
| Alloy 904L | Welded | 31 | 0, 0 |
| Alloy 20Cb-3 | Base | 20 | 0, 0 |
| Alloy 20Cb-3 | Welded | 23 | 0, 0 |
| 316L Stainless | Base | 46 | 0, 0 |
| 316L Stainless | Welded | 47 | 0, 0 |

*Maximum pit depth values given for both specimen faces.

## TABLE 8. PETERSBURG STATION CORROSION DATA

FGD Scrubber - D Module Presaturator
(7-Month Exposure)

| Alloy Exposed | Specimen Type | Weight Loss (mg) | Max Pit Depth* (mils) |
|---|---|---|---|
| Grade 2 Titanium | Base | 0.0 | 0, 0 |
| Grade 2 Titanium | Welded | 0.0 | 0, 0 |
| Grade 12 Titanium | Base | 0.0 | 1, 1 |
| Grade 12 Titanium | Welded | 0.0 | 1, 1 |
| Alloy 625 | Base | 102 | 1, 2 |
| Alloy 625 | Welded | 189 | 4, 1 |
| Alloy 904L | Base | 241 | 7, 4 |
| Alloy 904L | Welded | 293 | 6, 4 |
| Alloy 20Cb-3 | Base | 363 | 3, 4 |
| Alloy 20Cb-3 | Welded | 283 | 7, 3 |
| 316L Stainless | Base | 548 | 7, 5 |
| 316L Stainless | Welded | 345 | 5, 7 |

*Maximum pit depth values given for both specimen faces.

all stainless steel and nickel-base alloys tested experienced measurable weight loss, which was generally the result of pitting and some Teflon®-metal crevice attack. Pit depths ranged from 1-7 mils, with the 625 alloy exhibiting the least weight loss. In contrast, both titanium alloys demonstrated excellent corrosion resistance with negligible localized attack.

## PLEASANTS STATION CORROSION DATA

After 6.25 months, nickel-base and titanium alloy coupons exposed to the mixing/breech zone at Pleasants Station FGD scrubber revealed very mild surface pitting (~1-4 mils in depth). As presented in Table 9, pit penetration amounted to almost 15 mils for 904L stainless steel. The extent of pitting, judged with respect to weight loss, indicates that both titanium alloys suffered the least degree of overall attack, followed closely by the 625 alloy. Surprisingly, C-276 coupons suffered similar metal losses as the 904L coupons, apparently caused by additional general corrosion of the nickel alloy.

## DICKERSON STATION CORROSION DATA

Table 10 outlines data collected after a 7-month exposure at the base of the particulate scrubber stack. Clearly, Titanium Grades 2 and 12 proved to be totally resistant. The 625 and 904L alloys, however, experienced severe pitting and some Teflon®-metal crevice attack. Pits penetrated almost one-third of the thickness of sheet samples. The C-276 alloy exhibited significant weight loss in the form of shallow surface pits associated with apparent deposit and gasket-metal crevice corrosion. Visual examples of this diverse corrosion behavior of high-performance alloys are presented in Figure 10.

## SUMMARY OF HIGH-PERFORMANCE ALLOY CORROSION RESISTANCE IN SCRUBBER OUTLET DUCTS

A consistent trend in relative alloy corrosion resistance is apparent among all power plant scrubber outlet duct exposures evaluated in this study. Based on coupon weight loss, maximum pit depth, and Teflon®-metal crevice attack, the ranking of alloy resistance is:

Titanium Grades 2 and 12 > C-276 > 625 > 904L

Both titanium alloys were immune to Teflon®-metal crevice attack, while resisting pitting in all mixing zone and breech duct exposures. The C-276 alloy was subject to finite crevice corrosion and pitting attack in several outlet duct areas, and was generally much more resistant than the 625 alloy. This was particularly evident in the closed-loop scrubber mixing zone at the R. D. Morrow Sr. Station. Heavy pitting was characteristic of the 904L alloy in most outlet duct areas tested. The venturi particulate scrubber stack exposure at the Dickerson Plant produced exceptionally high rates of localized attack on these nickel and stainless alloys. The two open loop FGD scrubber outlet duct exposures at the Petersburg and Pleasants Stations, produced less

## TABLE 9. PLEASANTS STATION CORROSION DATA

FGD Scrubber - Mixing Zone
(6.25-Month Exposure)

| Alloy Exposed | Specimen Type | Weight Loss (mg) | Weight Loss Avg | Max Pit Depth* (mils) |
|---|---|---|---|---|
| Grade 2 Titanium | Base | 554 | 557 | 1.9, 1.5 |
| Grade 2 Titanium | Base | 559 | - | 1.9, 3.0 |
| Grade 2 Titanium | Welded | 567 | - | 4.1, 2.2 |
| Grade 12 Titanium | Base | 549 | 568 | 1.9, 2.0 |
| Grade 12 Titanium | Base | 587 | - | 3.5, 3.0 |
| Grade 12 Titanium | Welded | 528 | - | 4.1, 2.0 |
| Alloy C-276 | Base | 1,424 | - | 1.3, 1.3 |
| Alloy C-276 | Welded | 1,351 | - | 4.8, 2.8 |
| Alloy 625 | Base | 613 | - | 1.7, 1.7 |
| Alloy 625 | Welded | 619 | - | 1.3, 1.9 |
| Alloy 904L | Base | 1,243 | - | 9.3, 11.7 |
| Alloy 904L | Welded | 1,145 | - | 14.6, 5.2 |

*Maximum pit depth values given for both specimen faces.

## TABLE 10. DICKERSON STATION PARTICULATE FLUE GAS SCRUBBER CORROSION DATA

Base of Stack Attached to Drain
(7-Month Exposure)

| Alloy Exposed | Specimen Type | Weight Loss (mg) | Max Pit Depth* (mils) |
|---|---|---|---|
| Grade 2 Titanium | Base | 0.0 | 0, 0 |
| Grade 2 Titanium | Base | 0.0 | 0, 0 |
| Grade 2 Titanium | Welded | 0.0 | 0, 0 |
| Grade 12 Titanium | Base | 0.0 | 0, 0 |
| Grade 12 Titanium | Base | 0.0 | 0, 0 |
| Grade 12 Titanium | Welded | 1.0 | 0, 0 |
| Alloy C-276 | Base | 685 | 8, 3 |
| Alloy C-276 | Welded | 461 | 14, 5 |
| Alloy 625 | Base | 2,508 | 39, 34 |
| Alloy 625 | Welded | 2,611 | 33, 22 |
| Alloy 904-L | Base | 3,827 | 31, 32 |
| Alloy 904-L | Welded | 4,802 | 29, 34 |

*Maximum pit depth data given for both specimen faces.

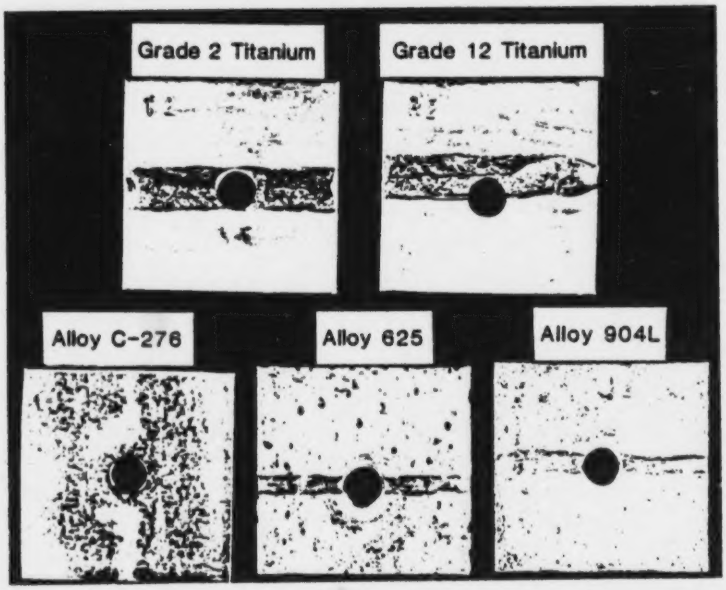

Figure 10. Comparison of various high-performance alloy coupons exposed at the base of the scrubber stack at the Dickerson Station.

distinction among high-performance alloys tested, probably the result of lower operating chloride levels.

## DISCUSSION

### TITANIUM ALLOY PERFORMANCE IN SCRUBBER OUTLET DUCTS

Titanium's apparent excellent resistance to FGD scrubber environments has been reported in a few previous field studies, and is, thus, not totally unexpected. Tice(20) included C.P. titanium in a spool rack exposure program in three types of FGD limestone slurry scrubbers. These exposures included absorber and outlet duct zones in flooded disc, venturi-absorber, and smelter gas scrubbers. In all exposures, including reheat zones, titanium exhibited no evidence of general or localized attack.

Rice and Burford(21) evaluated titanium in various municipal refuse incinerator flue gas scrubbers, which employ recycled water as the absorbing media. Exposures included zones before and after the absorber mist eliminator, including outlet duct and stack. Titanium proved to be totally immune in all tests and was judged to be the most reliable material evaluated for outlet duct/stack service. C-276 and 625 alloys both experienced pitting and crevice attack in several outlet duct exposures.

Consideration of the acidic oxidizing chloride nature of scrubber duct condensate as the basis for corrosive attack may well explain the observed behavior of titanium in these tests. Titanium is known to be extremely resistant to general corrosion and pitting in aqueous chlorides over a wide pH range and to very high temperatures.(24,25) In chloride brines, for example, titanium has anodic pitting potentials in excess of +1 volt (vs. Ag/AgCl reference) to temperatures greater than 200°C(26,27,28) and, thus, would not be expected to spontaneously pit under anticipated scrubber conditions. Exposures of titanium alloys to boiling ferric chloride, cupric chloride, $O_2$ or $Cl_2$-saturated brine, and other oxidizing chloride solutions similarly reveals excellent resistance to general and pitting attack.(25,29) Dissolved oxidizing species (cathodic depolarizers) are well known to provide passivation of titanium in normally aggressive reducing acid chloride and sulfate environments.(30)

Laboratory studies performed by Koch and Beavers(22) in a simulated outlet duct environment correlates with in situ results with titanium alloys. In this aerated "wet fog" test containing 5,000 ppm chlorides, Titanium Grades 2 and 12 experienced no general, crevice or pitting corrosion after the 1,000-hour test period. Thomas and Bomberger(23) similarly investigated resistance of several titanium alloys to boiling simulated scrubber solutions containing a wide range of chlorides. Corrosion resistance of these alloys proved to be excellent to fairly low pH's, often exceeding resistance of the highly alloyed nickel-base alloys studied.

Attempts by Battelle researchers to simulate scrubber outlet duct media in laboratory tests(12) strongly suggest that the actual complex scrubber duct environment cannot be adequately represented as a basic mixture of HCl, $CaCl_2$, $H_2SO_4$, and fluorides. This is indicated by the very high general corrosion rates reported for stainless, nickel and titanium alloys in the referenced study, which are not representative of field experience with scrubber duct materials. Since significant levels of chlorides and fluorides are present in both outlet duct condensate and ducting deposits,(18) additional factors are obviously involved that prevent corrosion of titanium under these acidic conditions. This is especially apparent considering titanium's lack of resistance to pure, hot HF and/or HCl solutions.

The presence of flyash in simulated scrubber liquors has been demonstrated to be a significant factor in explaining titanium's resistance in aggressive, hot, acidic chloride/fluoride environments. In this regard, Thomas and Bomberger(23) reported that small additions of flyash inhibit attack of various titanium alloys to much lower pH, particularly when fluorides are present. Explanations of this behavior are based on the silicon, aluminum, and calcium content of the flyash. It is theorized that these species reduce free fluoride ion activity by combination to form insoluble compounds or soluble complexes.

Titanium's resistance to deposit crevice corrosion, evident in field outlet duct exposures, also requires explanation. Susceptibility of titanium to crevice attack in aqueous chloride media increases with decreasing pH and increasing temperature, as shown in Figure 11.(25) From this figure, one would infer the probability of occurrence of C.P. titanium crevice corrosion under deposits in these low pH chloride exposures. However, the major presence of iron in both flyash(23) and ducting deposits(18) may be a key factor.

The high oxygen partial pressure in the flue gas would insure oxidation of any ferrous species to the ferric ($Fe^{+3}$) form. This ferric ion, as a strong cathodic depolarizer in acidic solutions,(25) stabilizes the oxide film on titanium, rendering it immune to attack from both acidic condensate and surface deposits. Since the ferric compound is an integral part of ducting deposits, under-deposit attack(29) cannot initiate. Further laboratory studies are necessary to substantiate these explanations.

In summary, the excellent performance of Titanium Grades 2 and 12 in the scrubber outlet ducts evaluated appears to be consistent with the oxidizing nature of ducting liquors and solids. The significant presence of oxygen and ferric species may explain passivation of titanium in hot acid ducting condensates, with flyash components possibly providing inhibition to fluoride attack.

## PERFORMANCE OF HIGHLY ALLOYED STAINLESS AND NICKEL ALLOYS IN SCRUBBER OUTLET DUCTS

The nature of localized attack observed on the 904L, 625, and C-276 alloys evaluated in these outlet duct field tests correlates very well with parallel in situ studies and actual service experience. This is, perhaps, most apparent in reported R. D. Morrow Sr. closed-loop scrubber exposures where chlorides, at levels an order of magnitude greater than in single pass systems, accentuate marginal differences between high performance alloys.

At the R. D. Morrow station, reported operating experience with Hastelloy G scrubber ducting revealed extensive pitting throughout mixing and breech duct zones.(3,9,14,16,18) Test sheet panels of 625 and C-276 alloys in the mixing zone were reported to have incurred pitting(9) and crevice corrosion,(14) respectively. Spool rack data generated in this zone indicate weld metal pitting of Alloy 625, with heavy pitting of the 904L alloy.(9) Maximum pit depths of 5-7 mils are similarly reported for 625 and 904L alloy coupons in an outlet duct exposure near the stack.(18) These findings, similar to the data presented herein, suggest a parallel ranking of stainless/nickel alloy corrosion resistance based on the (molybdenum + chromium) alloy equivalence.

Significant localized attack of high performance nickel/stainless alloys in scrubber outlet ducts has not been limited to closed-loop scrubber systems. At the Dallman and Laramie River Stations, Paul and Ross(17) have reviewed the extensive pitting and crevice attack experienced on Alloy 904L outlet ducting. Subsequent spool rack tests in the Dallman scrubber have shown deep localized attack with 904L and G alloys, incipient pitting of Alloy 625 weldments, and general immunity of Alloy C-276. Field coupon exposures at CILCO's Duck Creek No. 1 system have similarly indicated that all highly alloyed materials tested, with the exception of Alloy C-276, exhibit significant outlet duct pitting corrosion.(9)

Anderson(11) concludes that nickel-base alloys containing 9-16% molybdenum are required for the severe corrosive outlet duct condensate zones associated with limestone FGD scrubbers. In his survey of field outlet duct spool rack data, however, several cases of severe localized attack ($\leq$7 mils in depth) of Alloy 625 and C-276 coupons in FGD scrubber mixing zones suggest that even the most resistant nickel alloys are not always adequate. As expected, Alloys 904L and G exhibited heavy pitting.

Laboratory screening tests of highly alloyed stainless steel and nickel alloys in simulated $SO_2$-scrubber environments support the ranking of alloys observed, in addition to implicating species primarily responsible for the localized attack. Several oxidizing acid chloride screening tests conducted by Silence and Manning(8,9) predict critical pitting and crevice corrosion temperatures for various nickel-containing alloys. The oxidizing NaCl-HCl test exposures (involving 4%NaCl + 0.1%$Fe_2(SO_4)_3$ + 0.01MHCl), for example, reveal that pitting and crevice corrosion will occur respectively at approximately 100°C and 25°C for Alloy 625, and at 45°C and 20°C for Alloy 904L. The C-276 alloy appears to suffer crevice attack at temperatures as low as 80°C under these acidic oxidizing conditions. In ambient 10% ferric chloride exposures, light pitting is noted for the 625 alloy, while very heavy pitting is observed on the 904L and G alloys.(8)

Hibner and Ross(4,6,19) compared extensive laboratory and field test corrosion data, demonstrating that localized attack occurs on Alloys 625, G and 904L at chloride levels as low as 1,000 ppm in lower pH $SO_2$-scrubber environments. The additional presence of dissolved fluorides in FGD scrubber duct liquors was implicated in synergistically accelerating localized chloride corrosion.(18,19)

In summary, previous laboratory and field exposure tests predict the pitting and crevice corrosion observed on the highly alloyed nickel/stainless steel alloys evaluated in this spool rack study. The hot, oxidizing acid chloride character of the FGD outlet duct environment appears to adequately explain the extensive localized attack observed on these alloys, particularly at higher chloride levels found at the R. D. Morrow Sr. Station (closed loop) scrubber. Interestingly, the same species responsible for maintaining titanium alloy passivity in acidic outlet duct environments (i.e., $O_2$ and $FeCl_3$), appear to be very deleterious to corrosion resistance of nickel and ferrous alloys in the presence of chlorides.

## ALLOY PERFORMANCE IN FGD SCRUBBER INLET QUENCH DUCTS

The two scrubber inlet quench exposures evaluated in this study revealed significant variations in alloy performance. The open loop (low chloride) inlet presaturator at the Petersburg Station produced an overall ranking of high performance alloy corrosion resistance similar to that summarized for outlet ducts:

Titanium 2, 12 > 625 > 904L ( > 20Cb-3 > 316L)

The inlet quench exposure at the closed loop (high chloride) R. D. Morrow Sr. Scrubber No. 1, however, resulted in severe localized attack on both titanium alloys, with significantly less attack on Alloys C-276, 625 and 904L.

The wet/dry interface of the inlet quench duct potentially represents the most corrosive zone in the scrubber, resulting from very high temperatures (143-177°C), very low pH, and oxidizing species associated with incoming hot, acidic flue gases and flyash. Very few materials can resist localized attack under these conditions, especially when scrubber liquor chloride levels become significant.

The localized attack observed on these titanium alloys is not unexpected, considering inlet quench conditions at the R. D. Morrow Sr. Plant. Specifically, deposit crevice corrosion is predicted in low pH chloride environments when temperatures lie in the 121-177°C range, as shown in Figure 11. Calcium sulfate (or sulfite) deposits which form at the wet/dry inlet interface can provide viable crevice sites for attack. The calcium carbonate and ferric chloride containing

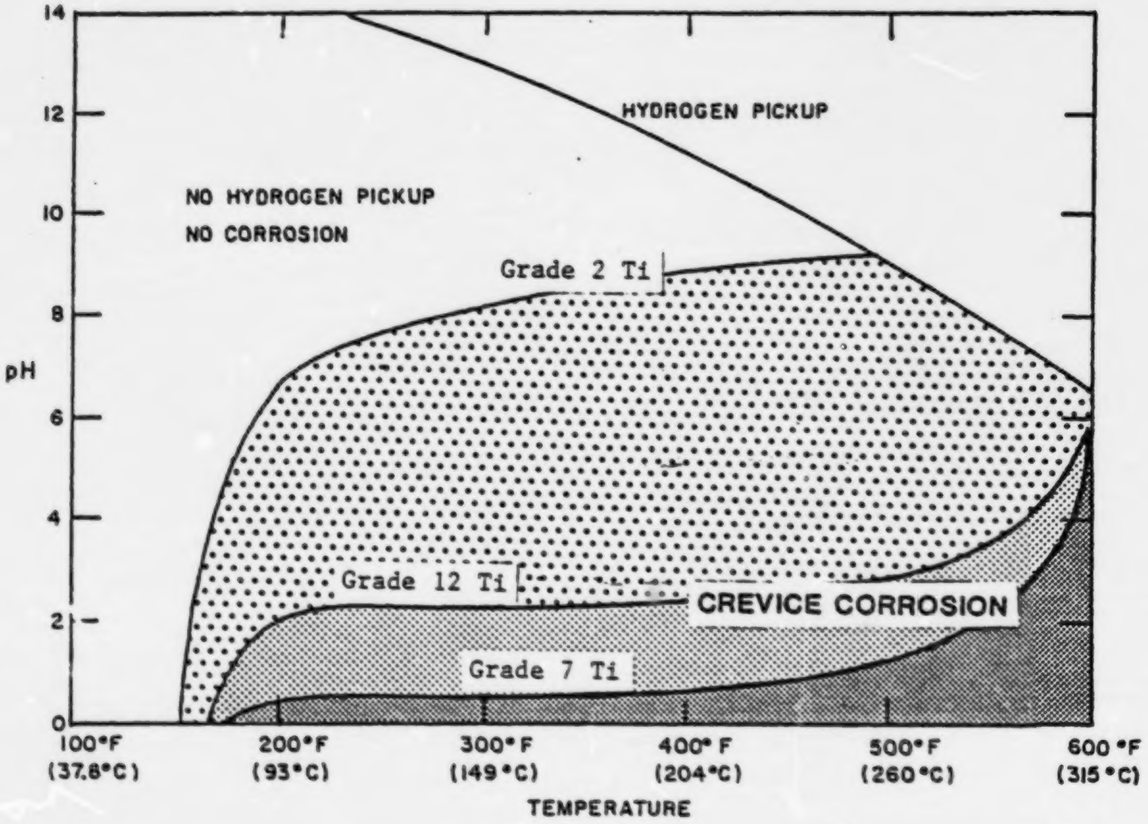

Figure 11. Crevice corrosion of titanium in saturated NaCl brines.

components of inlet quench deposits, however, would not be expected to create crevice problems for titanium due to the alkaline and oxidizing character of these components, respectively.

Assuming that this chloride crevice attack mechanism is in effect, one would predict that the Ti-Pd (Grade 7 Titanium) alloy could resist these low pH, high-temperature conditions (Figure 11). If, however, fluorides are integral to this corrosion mechanism, the Ti-Pd alloy probably would suffer similar attack. Current in situ inlet quench exposures at R. D. Morrow Sr. Scrubber No. 1 may soon shed some light on this mechanism.

The localized attack exhibited by nickel-base and stainless steel alloys in the R. D. Morrow Sr. inlet quench duct correlates with that reported for previous field and service experience. Silence and Manning(9) describe "saucer-shaped" depressions, up to 10 mils deep, on Alloy C-276 sheet liners in the wet/dry zone of the R. D. Morrow Sr. inlet quench duct, similar to the shallow pits noted in this study (Figure 8). At this location, Hastelloy G previously suffered severe localized attack in service.(8,18)

Severe pitting and crevice attack of Alloys 904L and 625 were reported at the Dallman and Laramie River Station quencher zones.(16,17) Similar performance with 904L occurred at Springfield City Utilities' Southwest 1 Station.(16) Anderson's review(11) of field corrosion studies in FGD limestone scrubbers further reveals examples of significant inlet quench pitting of Alloys 904L and G. These findings can also be explained by the low pH, oxidizing chloride conditions of the inlet duct, similar to effects discussed in the previous outlet duct review.

Curiously, for both inlet quench zones included in this study, net differences in maximum pit depth experienced by C-276, 625 and 904L alloys were quite small, in contrast to distinctive alloy differences produced during outlet duct exposures. This may be related to the alkaline $CaCO_3$ component of inlet quench duct deposits and also be influenced by positioning within the wet/dry interface zone.

In summary, C-276, 625 and 904L alloys experienced finite localized attack in the two scrubber inlet quench zones evaluated in this study. The titanium alloys, however, exhibited diverse behavior, apparently related to deposit crevice corrosion in the high chloride, closed-loop scrubber system. The variable behavior observed may be attributable to spool rack positioning in the wet/dry zone of the inlet quench duct, the chemical nature of inlet duct deposits formed, and chloride (and/or fluoride) scrubber levels.

## CONCLUSIONS

(1) Field corrosion tests, of up to nine months duration, reveal the following ranking of high-performance alloys in outlet duct exposures:

Titanium Grades 2 and 12 > C-276 > 625 > 904L

This was particularly evident in the corrosive closed-loop scrubber system at the R. D. Morrow Sr. Plant, and the venturi particulate scrubber at the Dickerson Station.

(2) The superior resistance of titanium alloys compared to the nickel/stainless steel alloys tested in outlet ducts is very well explained by the acidic oxidizing chloride character of outlet duct condensate and solids. Ferric compounds found in flyash, in conjunction with oxygen from flue gas, may be responsible for passivation of titanium under these acidic conditions. More laboratory testing is necessary to substantiate these effects.

(3) Wet/dry interface zones in two inlet quench duct exposures reveal variable performance of titanium alloys. High temperature deposit crevice corrosion is indicated, and may require Ti-Pd (Grade 7 Titanium) alloy when scrubber chlorides are high. C-276, 625 and 904L alloys consistently experienced localized attack involving pit depths of 1 to 10 mils.

(4) Based on this preliminary field test data, titanium is recommended for serious future consideration as a cost-effective candidate material for problem areas of FGD scrubber systems.

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## SESSION 4: DRY FURNACE ABSORBENT INJECTION

Chairman: Randall E. Rush
Flue Gas Treatment and Water
Quality Section
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# RESULTS FROM EPA's DEVELOPMENT OF LIMESTONE INJECTION INTO A LOW $NO_x$ FURNACE

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## INTRODUCTION

As discussed in previous papers (1,2), the Environmental Protection Agency (EPA) has been developing control technologies for $SO_x$ and $NO_x$ emissions. Because of the magnitude of, and the possible link between, such emissions from power plants and environmental problems such as acid rain, one focus of $SO_x/NO_x$ control has been combustion processes. Previously developed low $NO_x$ systems for coal combustion are being demonstrated, and methods for removal of $SO_x$ in these systems are under development. The primary method for $SO_x$ control is the use of Limestone Injection into a Multistage Burner (i.e., low $NO_x$ burner) which is abbreviated as LIMB. The objective of the EPA program is to develop LIMB and low $NO_x$ burner technology for both retrofit and new applications so that industry can demonstrate and commercialize this technology in the post-1986 time frame for both wall-fired and tangentially-fired boilers.

The LIMB program is an EPA effort to develop effective and inexpensive emission control technology for coal-fired boilers that will reduce $SO_x$ and $NO_x$. LIMB technology represents a low-cost alternative to currently available $SO_x$ control approaches; e.g., flue gas desulfurization, coal cleaning, and coal switching. LIMB technology is attractive if coal combustors must be controlled to minimize emissions acid rain precursors because LIMB is easily retrofitted to large and small coal-fired boilers, is lower in cost than any available alternative, and can control both $SO_x$ and $NO_x$ -- the two major acid rain precursors. The technical goals of the program are: 1) for retrofit applications, achieve 50-60% reduction of both $SO_x$ and $NO_x$ from uncontrolled levels; 2) for new systems, achieve 70-80% $NO_x$ and 70-90% $SO_x$ reduction from uncontrolled levels; and 3) for both retrofit and new systems, achieve the above goals at costs at least $100/kW less than the major technology alternative, flue gas desulfurization.

Given these goals, the program was structured to address major aspects of LIMB development and application with consideration to three issues. First, that the existing boiler population is approximately 45% wall-fired and 45% tangentially-fired. Second, that the program must define variables governing sulfur capture, impact on particulate control equipment, and impact on boiler operation (including potential problems with slagging and fouling). There is also the question of ultimate disposal or reuse of the limestone modified fly ash. Lastly, that there is the need to be able to extend development results to boiler design which can only be verified by a demonstration.

To achieve the program goals, the EPA has organized a program consisting of:

1. Basic understanding of mechanisms and kinetics.
2. Systematic small bench and pilot scale development.
3. Large scale pilot testing.
4. Process and systems analysis.
5. Field application to representative boilers.

Results from item 1 have been discussed in detail in other papers (3,4) and a summary of conclusions is provided under Background, below. Results from items 3, 4, and 5 are at a very early stage which do not provide a basis for significant comment. Consequently, the subject of this paper is item 2; namely, results from bench and pilot scale testing.

## BACKGROUND

The purpose of this paper is to update the status of LIMB development from the time of the paper presented at the previous FGD meeting (May 1982 in Florida).

A quick review of the history of the limestone injection/LIMB process follows. From 1968 to 1971, dry sorbent injection was evaluated. General conclusions were that there was insufficient $SO_x$ removal (15-50%), that thermal deactivation (deadburning) of the sorbent was a major problem, and that power plant operational problems were possible including fouling in the convective passes and loss in the efficiency of the electrostatic precipitator. In the summer of 1979, EPA pilot plant tests indicated the possibility of 70% removal of $SO_x$ with limestone injection through low-$NO_x$ burners at reasonable alkali to sulfur ratios. Subsequently, the LIMB program was initiated (October 1980). In-house experiments started with a program to define mechanisms and kinetics. Conclusions from that work include: 1) surface areas formed during rapid limestone calcination in the dispersed phase are in the range of 50-60 $m^2/g$, 2) there is a strong relationship between surface area and lime reactivity, and 3) calcination kinetics can be expected to have a significant effect on $SO_x$ capture using limestone injection.

During recent years EPA has proceeded with development on a wide range of furnaces (30 kWt to 30 MWt) at five locations using primarily wall-fired pulverized coal combustion technology. However, other combustion systems are being studied; e.g., tangential pulverized coal combustion and spreader stoker coal combustion. Results presented below are from wall- and tangentially fired furnaces of a small pilot size (0.3 to 0.5 MWt). The wall-fired unit is the boiler simulator furnace (BSF), at Energy and Environmental Research Corporation's plant in Irvine, California. The tangentially fired furnace is at Acurex Corporation's plant in Mountain

View, California. A detailed description of these furnaces has been published (1). An extremely important feature of these furnaces is that the gases leaving the combustion zone pass through a temperature profile that was designed to simulate the range of temperature profiles in a coal-fired, steam-electric generating plant. It was anticipated that the temperature profile would be important in the reaction between limestone and $SO_x$ in the flue gas.

A presentation at the May 1982 EPA symposium noted that very high $SO_x$ captures (70-80% at 2X stoichiometric) were possible using the BSF fired on natural gas. At that time it was suspected that there was an interaction between the sorbent and some component of coal which inhibited good performance of the sorbent during coal firing. In any case, the historical explanation of deadburning's causing poor performance was refuted because the natural gas firing conditions could be made to produce temperatures even higher than those in coal firing without loss of sorbent reactivity.

## RESULTS

To put effects of furnace and limestone injection options in context, the results will be discussed in three sections, corresponding to the critical steps for $SO_x$ control with limestone:

1. Limestone conversion to lime (with good reactivity).
2. Reaction of lime with sulfur species.
3. Thermal and chemical deactivation of lime.

## LIMESTONE CONVERSION TO LIME

Results for surface areas of three limes are shown in Figure 1. Data for most of these results were developed under EPA contract 68-02-2566 with Northrup Services, Inc. The limestones from which these limes were derived are all calcites (rhombohedral form of $CaCO_3$). The calcites called Vicron and El Dorado are both coarse grained; that is, the fundamental size of an individual crystallite is large (>50 µm). The marl by formation is a reprecipitated deposit and is fine grained (the grains are 1-3 µm). Surface areas have been determined by two methods: mercury porosimetry and the BET method. Most of the data shown in the Figure 1 are for batch calcination in a platinum crucible. Whether measured by BET or mercury porosimetry, the surface areas of limes prepared under soft-burning conditions (980°C for 2 hours) are in a range of 1 to 4 $m^2/g$. By searching combinations of calcination conditions and allowing as much as 30% to be uncalcined, it is possible to achieve surface areas an order of magnitude higher. However, the best surface area for the fine grained marl does not ever come close to the best surface areas for the coarse grained calcites. For the Vicron limestone tested under EPA contract 68-02-3633 with EERC, results under shock calcination conditions are also shown. For this calcination, the limestone was exposed to 1400°C for only a few milliseconds. This illustrates the high surface areas that can be achieved during very short calcination times although even higher surface areas have been reported elsewhere (3).

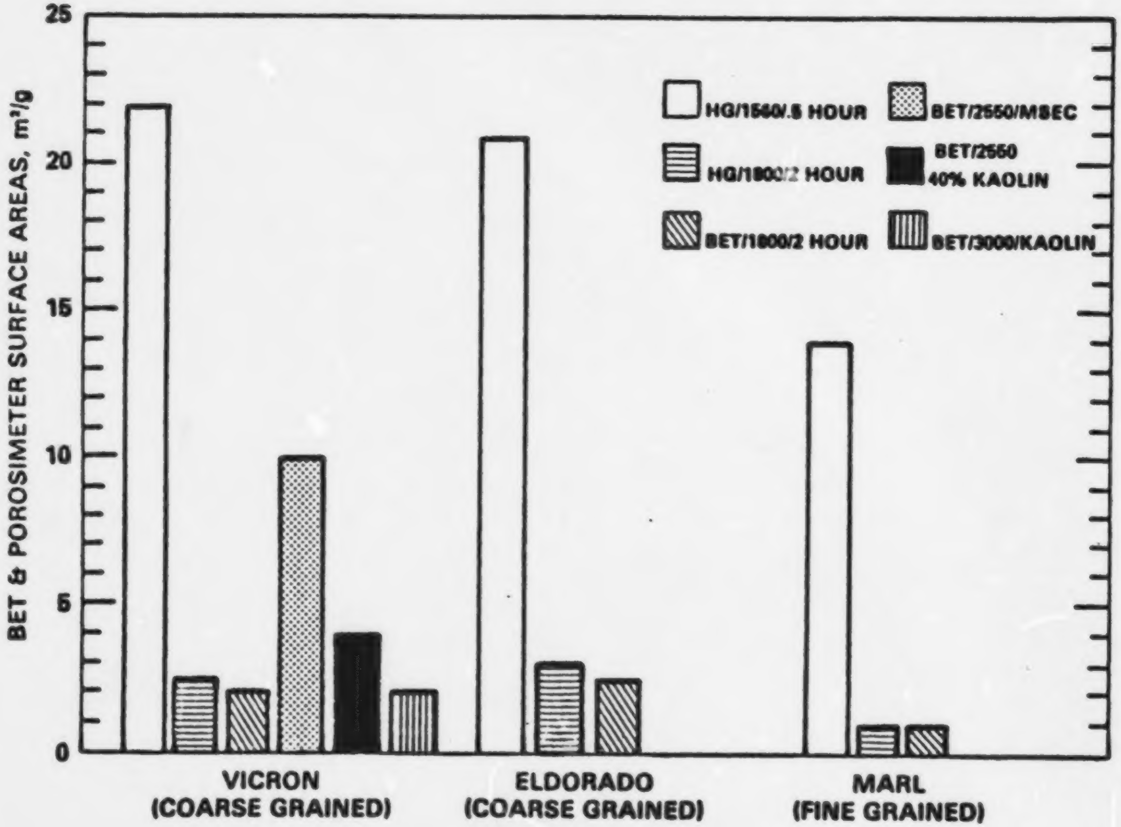

FIGURE 1. SURFACE AREAS FOR THREE CALCITES.

Since an important impurity in coal is kaolinite, it is interesting to note the effect of kaolin addition to limestone on the surface area of shock calcined Vicron. At 1400°C, the surface area is reduced by almost two thirds, and at 1650°C, the surface area is reduced to less than a fourth of that for the pure lime.

A comparison of the utilization of different $SO_x$ sorbents is given in Figure 2 for wall-fired propane (doped with $H_2S$) or pulverized coal combustion as derived from EPA contract 68-02-3921 with EERC. These data were taken from experiments on the BSF. In Figure 2, dolomite and hydroxide are compared as well as three calcites. With the knowledge that the hydroxide is inherently fine grained, the results for propane firing show that the calcium utilization for $SO_x$ capture with Vicron (coarse grained) is a third higher than that for fine grained sorbents. Moreover, the coarse particle Vicron (diameter about 11 $\mu$m) appears to perform better than the fine particle Vicron (diameter about 3 $\mu$m). The performance of dolomite is within the range of the other sorbents during propane firing.

The interaction between fuel type and sorbent type is shown in Figure 2. Note the changes in sorbent utilization in comparing propane firing and coal firing. The dolomite loses one third of its reactivity, and the calcites lose one half to two thirds of their reactivity.

Derived from EPA contract 68-02-3684 with Acurex, data for tangential firing with natural gas (doped with $H_2S$) are given in Figure 3. As before, the very finest particles do not give the best results, and one set of data implies that there is an optimum particle size.

## REACTION OF LIME WITH SULFUR SPECIES

As noted above, the capture of $SO_x$ should be favorable in a certain temperature range which is bounded above by decomposition of the product ($CaSO_4$) and below by slow kinetics. Also derived from EPA contract 68-02-3684 with Acurex, Figures 4 and 5 give some additional verification of the important effect of temperature profile. Figure 4 displays three temperature profiles that have been used in the tangentially fired furnace. These profiles start from a point approximately 2 m above the level of the burners so that the beginning temperatures in Figure 4 correspond to a residence time of 2.4 seconds at normal load. Changes in temperature profile were accomplished by modification to the placement and size of heat exchangers. For the overall temperature range displayed, note that the first profile has a precipitous drop in the middle of the range, while the third profile shows the most time in the middle of the range. Figure 5 gives the $SO_x$ capture during coal firing for these different temperature profiles. The first profile has less than half the $SO_x$ capture of the third profile, and the second profile has an intermediate performance.

Limestone can be injected at several locations for each type of furnace. For the tangential furnace, air is provided for combustion either with the coal, near the coal, or some distance above the level of coal injection, called primary air, lower auxiliary air, and overfire air, respectively.

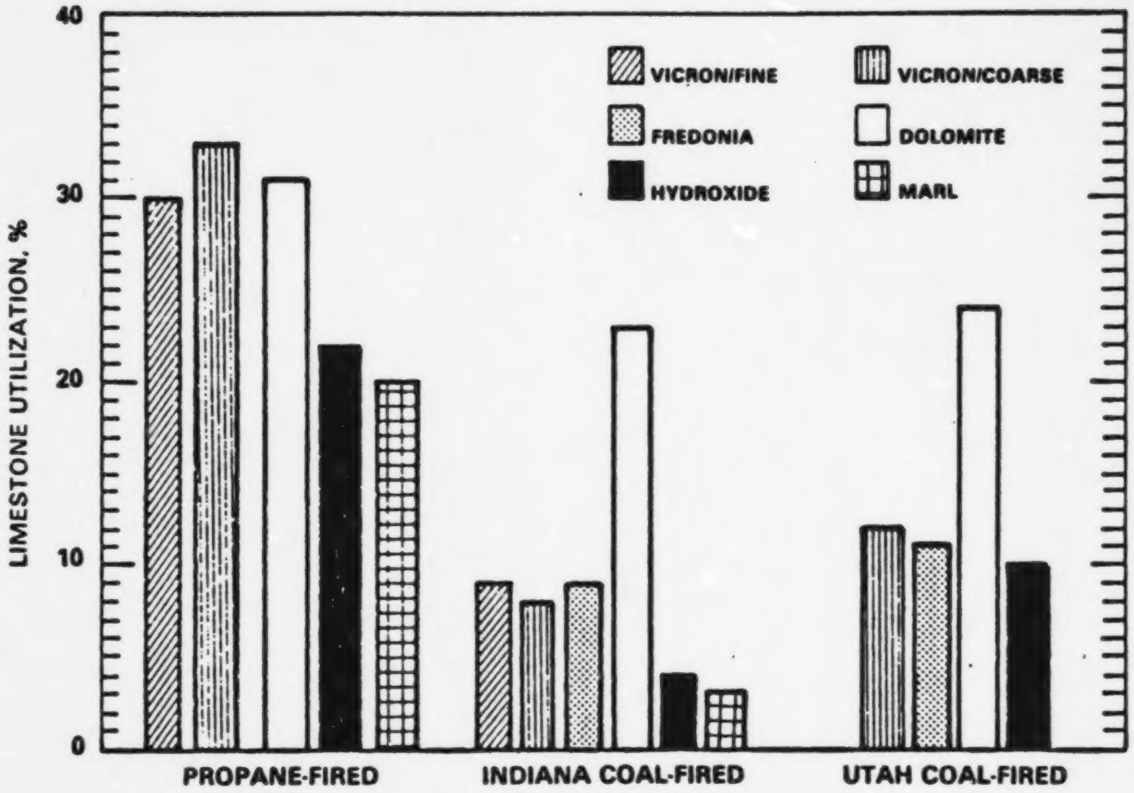

FIGURE 2. WALL-FIRED: SORBENT AND FUEL EFFECTS.

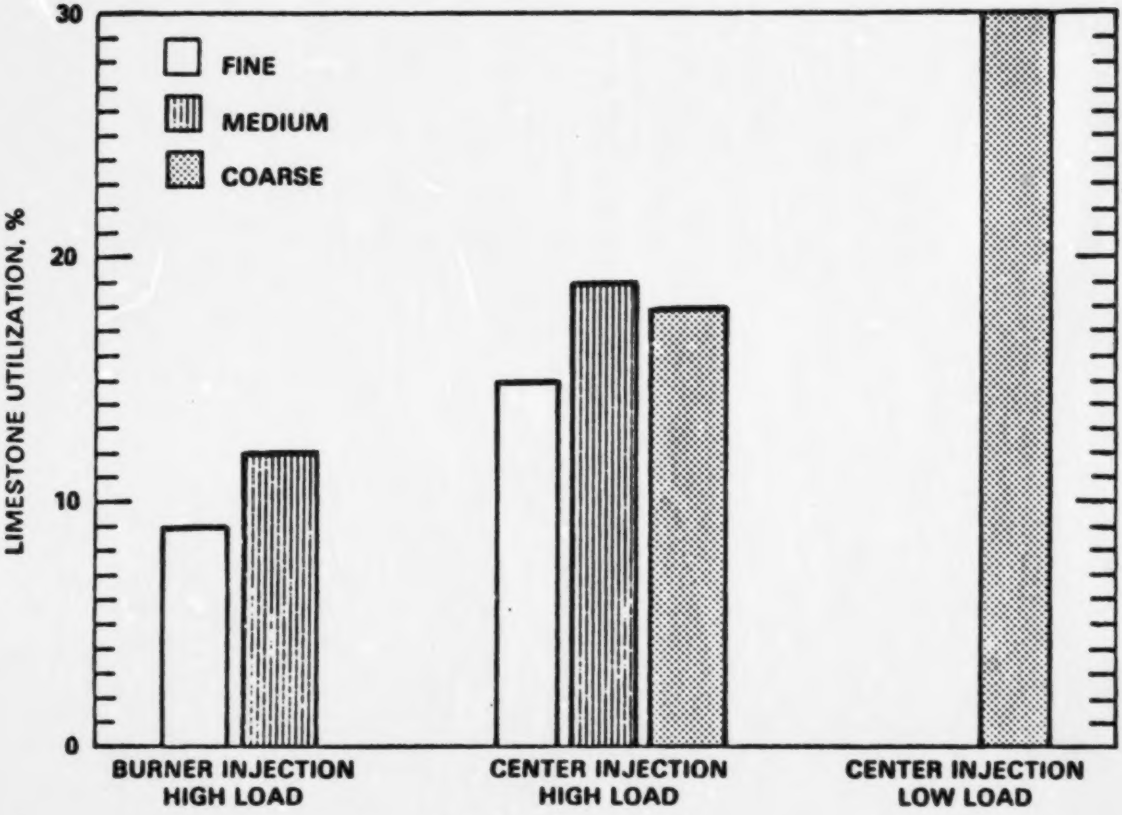

FIGURE 3. T-FIRING: PARTICLE SIZE EFFECT.

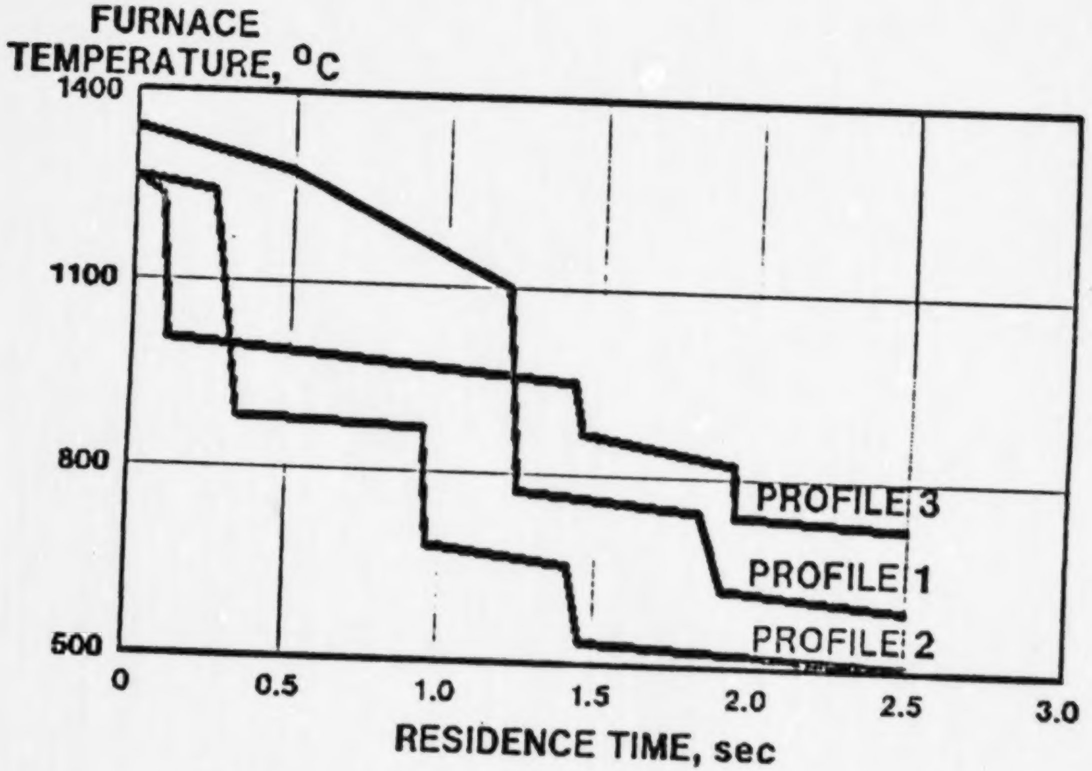

FIGURE 4. TEMPERATURE PROFILES IN T-FIRING.

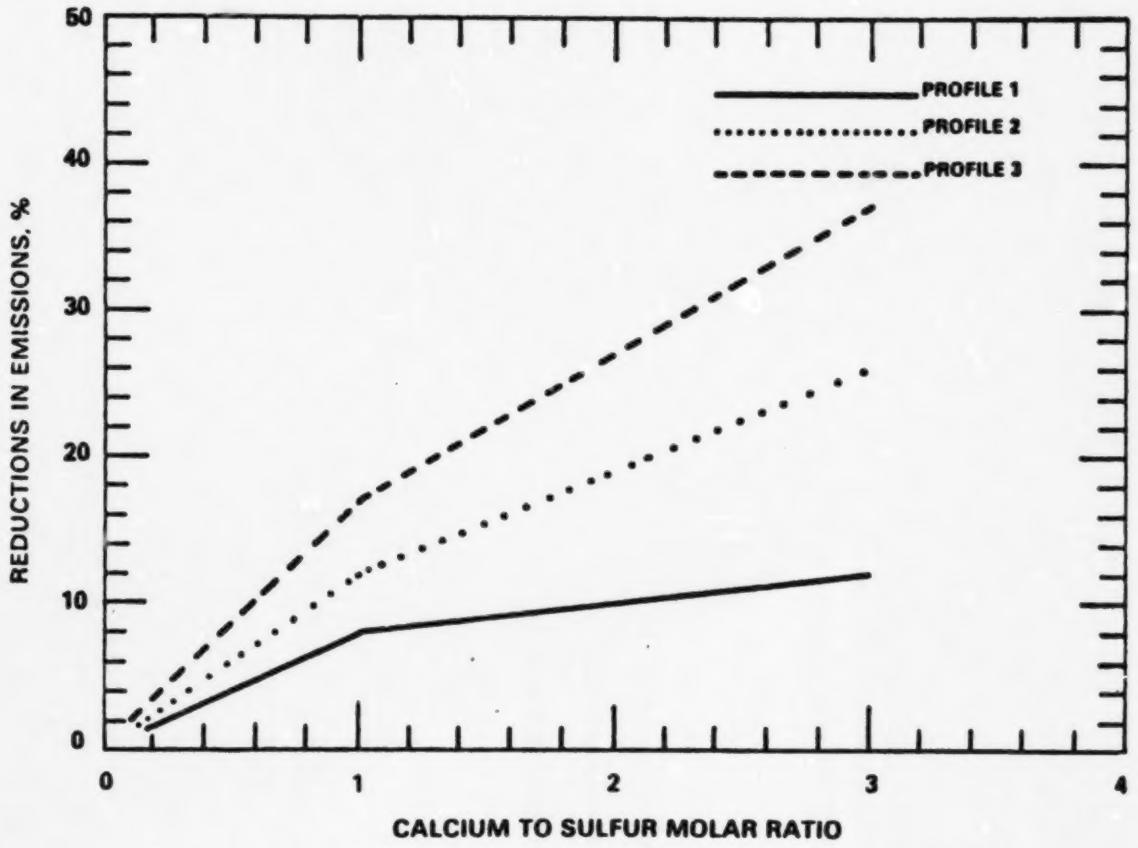

FIGURE 5. T-FIRING: TEMPERATURE PROFILE EFFECT.

All of these air injection locations have been used for limestone injection. However, a tangentially fired furnace introduces all of these air streams from the side (specifically, the corner) of the furnace. Because the tangentially swirling motion of the combustion gases could prevent even distribution of limestone injected from the side, an additional location (using a probe) was devised to inject limestone into the center of the furnace. A comparison of the $SO_x$ capture in the Acurex tangential furnace using these different injection locations is plotted in Figure 6. Injection with the coal gives the poorest result, and injection into the center, the best.

## THERMAL AND CHEMICAL DEACTIVATION OF LIME

Figure 7 demonstrates the effect of fly ash on lime reactivity in the BSF under EPA contract 68-02-2667 with EERC. Using natural gas as the fuel, the increase in fly ash addition results in a decrease in limestone utilization. This effect is also related to the limestone concentration as shown by the family of lines for utilization at different calcium to sulfur molar ratios. The decrease in utilization for a given fly ash addition is not as bad when the calcium to sulfur ratio is higher, but the absolute value of utilization is worse at higher calcium to sulfur molar ratios.

By firing the Acurex tangential furnace (EPA contract 68-02-3684) on natural gas and injecting fly ash, it was verified that this system also saw an effect of limestone and fly ash interaction on the $SO_x$ capture. Figure 8 shows the change in limestone utilization in collecting $SO_x$ when fly ash is added. The full range of fly ash addition spans from clean conditions to those similar to coal combustion. For center limestone injection, the limestone utilization is reduced by half. Data were not available for side injection over the whole range, but the rate of reactivity loss with fly ash addition is the same.

Besides adding fly ash to natural gas firing in the BSF, other compounds have been tried to narrow the range of mineral species which may cause a loss of limestone reactivity under EPA contract 68-02-3921 with EERC. In particular, bentonite and kaolin were used to determine the effect of silica or alumina on the performance of the limestone Vicron in capturing $SO_x$. An important result of that experiment is plotted in Figure 9 which shows a good inverse correlation between $SO_x$ capture and the alumina content of the inlet solids. This correlation draws together data from simple coal firing (Indiana coal), from fly ash addition (ash from a furnace called the Small Watertube Simulator or SWS), and from mineral matter addition (bentonite and kaolin).

# DISCUSSION OF RESULTS

## LIMESTONE CONVERSION TO LIME

Data shown under Results, above, suggest the possibility of very high surface area limes (>20 $m^2/g$) being present in the furnace for very short periods of time--certainly less than 1 second. Because $SO_x$ capture is a

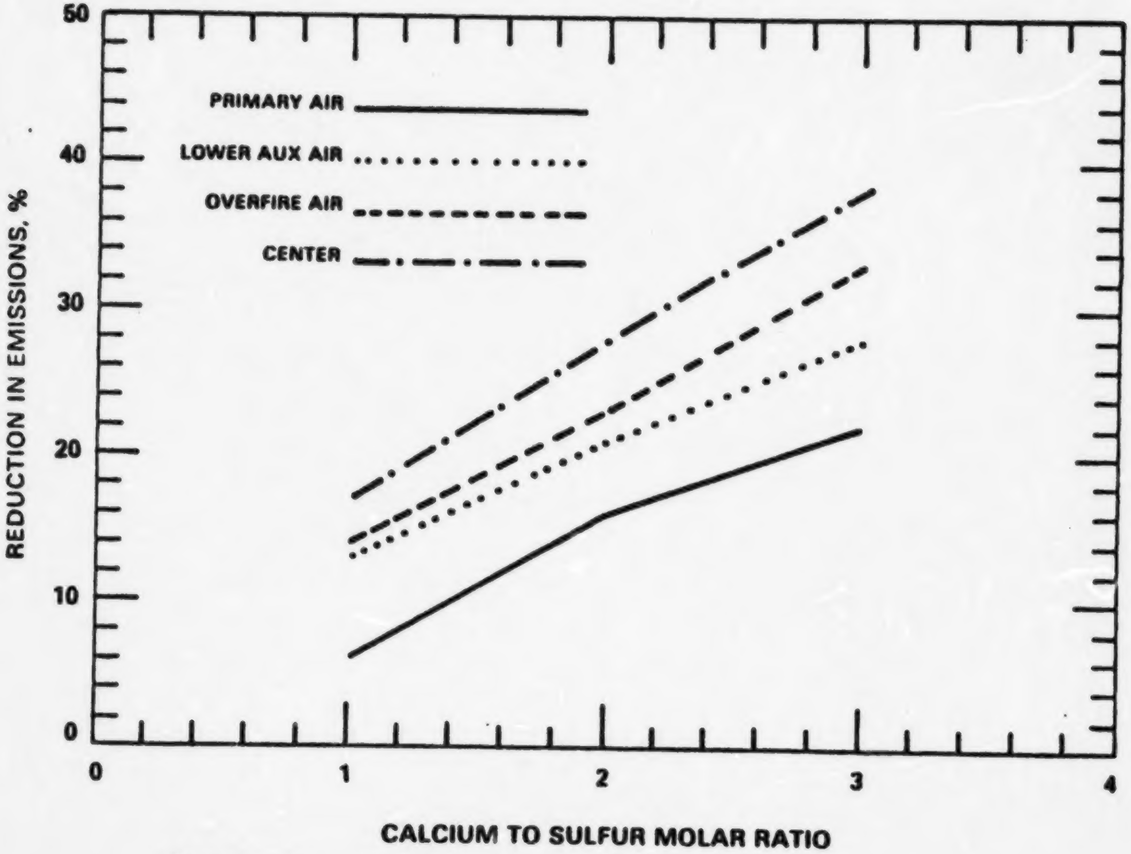

FIGURE 6. T-FIRING: INJECTION LOCATION EFFECT.

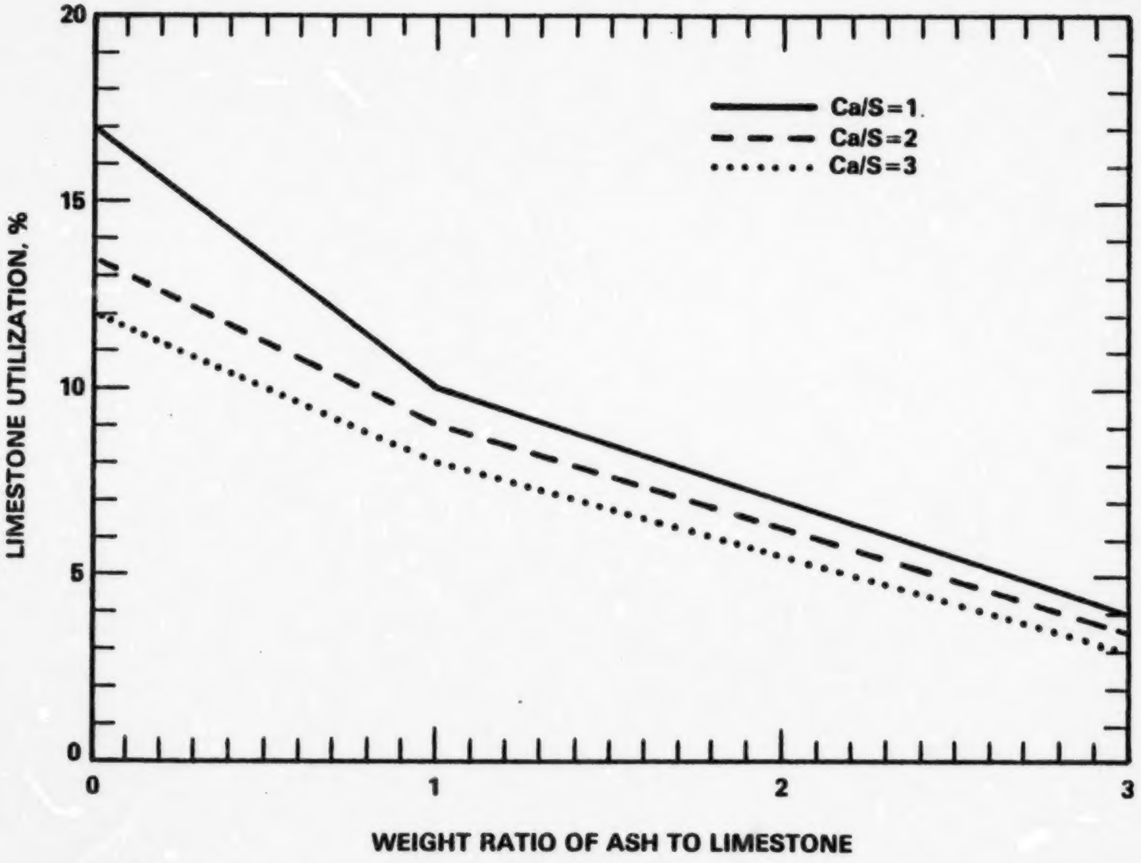

FIGURE 7. WALL-FIRING: FLY ASH EFFECT (FUEL = GAS)

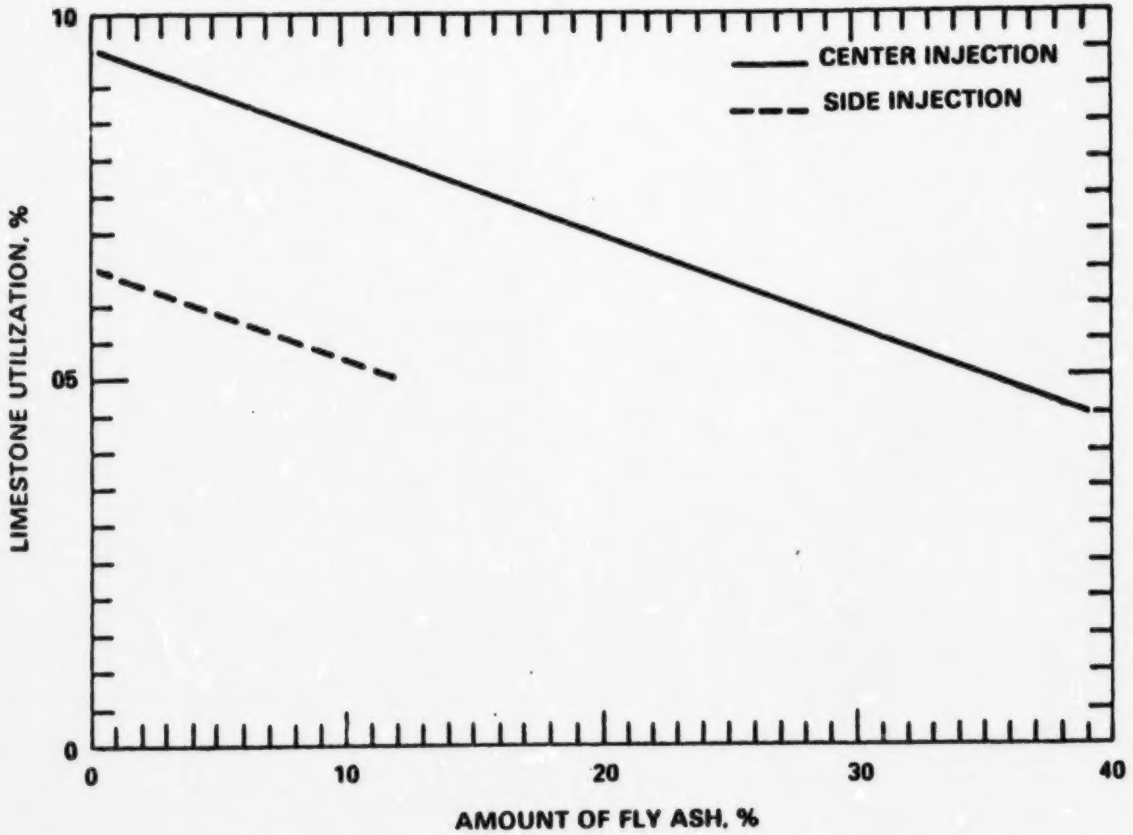

FIGURE 8. T-FIRING: FLY ASH EFFECT (FUEL = GAS).

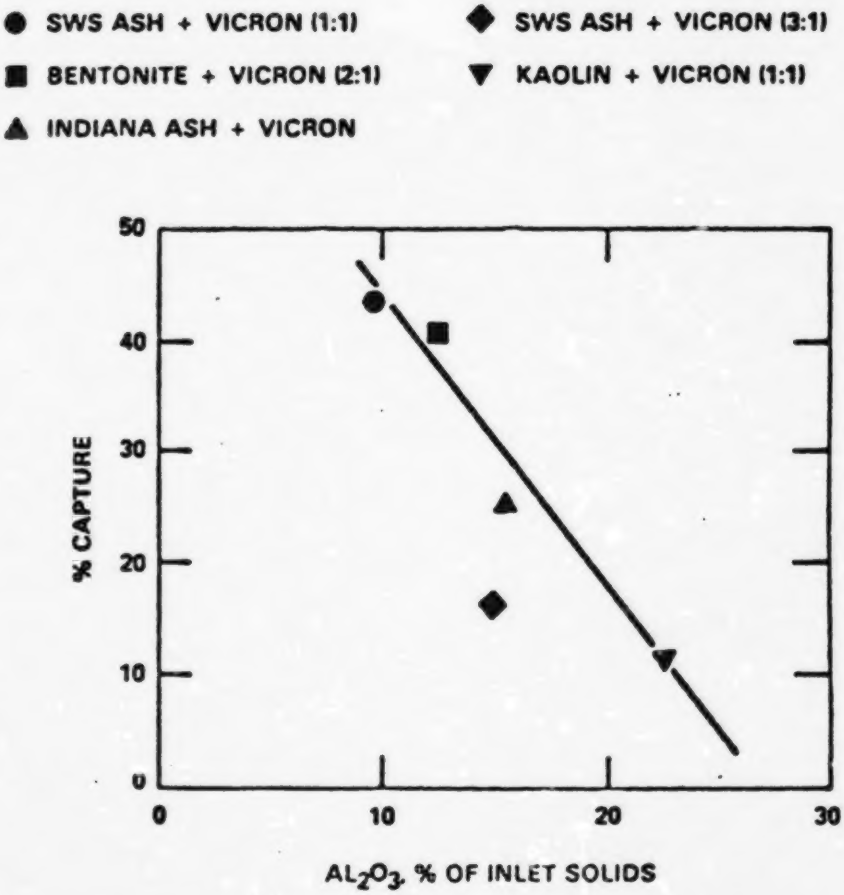

FIGURE 9. IMPORTANCE OF COAL MINERAL MATTER.

direct function of surface area, optimizing the presence of high surface area lime is vital. That this critical path can be controlling is demonstrated by the relative performance of the coarse and fine grained calcites. The coarse grained calcites achieve higher surface areas and show better $SO_x$ capture in furnace injection during propane firing. Similarly, the effect of particle size should be noted. As the original particle size is reduced, it is expected that the reactivity will be enhanced because of the greater surface area of the limestone. However, very small limestone particles may calcine too rapidly and may actually give smaller surface areas in their calcined forms than those of slightly bigger particles. Certainly, the data show that continued reduction of the limestone particle size may be detrimental, and an optimum limestone grind should be determined.

## REACTION OF LIME WITH SULFUR SPECIES

The presence and critical importance of an optimum temperature range has been discussed in the past. Current data show the strong effect of temperature profile, although the exact definition of the temperature range is not possible. If the tangential furnace temperature values are for bare thermocouples, the actual temperatures may be 100°C higher than shown in Figure 4. It would appear that the temperature range of interest is approximately 850 to 1300°C. The effect of different limestone injection locations provides different mixing conditions and different temperature profiles for calcination. The fact that center injection was superior to any of the side injection locations in the tangential furnace verifies that mixing is critical in this case. The variation in performance of the other injection locations suggests a shifting of the match between the availability of the very high surface area lime and the temperature range for the sulfation reaction. Because calcination is very rapid and the very high surface area would be available early in the calcination process, it is reasonable that the best performance for side injection should come from the overfire air location where the limestone quickly passes into the temperature range for sulfation.

## THERMAL AND CHEMICAL DEACTIVATION OF LIME

For both wall- and tangentially-furnaces, fly ash has a negative influence on limestone utilization. Because of a correlation of this negative influence with the alumina content, it may be supposed that the fly ash collides with the limestone, and low melting compounds of alumina and lime are formed which may flux the surface of the lime particle to a glassy nonporous sphere. The surface area data with and without kaolin addition demonstrate the negative effect of kaolin on the open structure of the sorbent. Questions that arise are how do the fly ash and lime particles collide, do the fly ash particles have to be sticky, and does the chemical nature of the sorbent (calcite vs dolomite) influence the reaction between alumina and the sorbent. The information in Figure 2 indicates some answers to these questions. Comparing the results for propane firing and those for Indiana coal firing, indicates the possibility of the influence of particle size. Specifically, the reduction in utilization for the coarse Vicron is worse than that for the fine Vicron. However, this is a small effect and must be considered because Vicron shatters during shock calcination to sizes an order of magnitude lower. The importance of a particle size effect would be to suggest that collision of the fly ash and lime depends on inertia (and thus size) differences. Again comparing the same two data sets, the marl and hydroxide--both fine in size--lose reactivity dramatically in switching from propane to coal firing, and the dolomite--coarse in size--retains much of its reactivity. Dolomite may also retain reactivity because the structure of its calcine may not be as easily blinded by surface reactions. Comparing the two coal data sets, indicates that the marl is much more reactive with Utah coal firing than with Indiana coal firing. This may be attributed to chemical deactivation because a change in fly ash size gives less interaction between fly ash and sorbent, or it may be attributed to limestone's conversion to lime because of a change in the peak temperature which affects calcination. Obviously at this point, more experiments are required to define the interaction of different sorbents with fly ash.

Future work will also address the general problem of minimizing the interaction of fly ash and sorbent. It is possible that some coals are less likely to produce troublesome fly ash. Consequently, several coals with different rank or mineral composition will be tested. Fly ash can also be minimized by use of a cleaned coal or a precombustor which removes slag before gases enter the main furnace. If aluminum oxide is the only problem, then coal cleaning could be optimized for its removal. Other approaches to the fly ash interaction problem involve the sorbent. The sorbent could be modified to allow its injection at a point where fly ash is no longer active. It is also possible that the sorbent could be modified to be protected from the fly ash.

## CONCLUSIONS

The success of $SO_x$ control with limestone injection will depend on the success of three critical steps:

1. Production of a highly reactive sorbent.
2. Favorable conditions for the sulfation reaction.
3. Avoidance of sorbent deactivation by interaction with fly ash.

For a given system, any one or more of these critical steps could be controlling; therefore, careful analysis of the data is required to identify the appropriate problem(s). The small pilot scale data for both wall- fired and tangentially fired furnaces have shown that failure in any of the above steps can reduce $SO_x$ capture by a factor of 2 or more. Without fly ash (firing gaseous fuel) and operating under reasonable furnace conditions, limestone utilizations as high as 40% have been achieved. At a calcium to sulfur molar ratio of 2, this means that 80% control is possible. Problems in any one of the critical steps will reduce this accordingly. For the last critical step--fly ash interaction-- specific approaches to a solution are under investigation, and minimization of this problem should be possible for most furnaces.

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# REVIEW OF EPRI RESEARCH ON FURNACE SORBENT INJECTION $SO_2$ CONTROL

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## ABSTRACT

Direct furnace injection of alkaline material is currently under development as a potential low cost $SO_2$ control approach for new and existing coal-fired boilers. Major developmental efforts now focus on 1) understanding process fundamentals, 2) process optimization for both new and retrofit applications and 3) the resolution of power plant impact issues and costs. Current and planned EPRI research projects in these areas are reviewed.

## INTRODUCTION

In the early 1960's the concept of direct sorbent injection into the furnace of a utility boiler originated as a means for reducing $SO_2$ emissions without involving utility companies in sophisticated chemical flue gas treatment systems. It was felt at the time that direct injection of limestone followed, for example, by wet particulate scrubbing was the least complicated and most economical procedure for meeting anticipated $SO_2$ as well as particulate removal requirements. However, various trials of this concept at laboratory furnaces and full scale utility boilers in the U.S., Europe and Japan, generally failed to demonstrate sufficient in-furnace $SO_2$ removal at practical sorbent to sulfur ratios. $SO_2$ removals during tests at utility boilers typically ranged from 15% to 40%, well below the target values of 70% to 90%. $SO_2$ removals were also highly dependent on the design and operation of the boiler as well as the type of sorbent and injection system used. The potential for adverse effects on boiler performance also surfaced during these early test programs. Most notably, increases in slagging and fouling of boiler heat transfer surfaces and degraded performance of electrostatic precipitator controls were reported. Because of the low and variable $SO_2$ removal efficiencies combined with boiler operational concerns, further process testing was abandoned by the early 1970's and the development of wet $SO_2$ scrubber systems became the primary focus of $SO_2$ control efforts. (1)

A variety of factors have contributed to the renewed interest in furnace sorbent injection. Foremost among these are the recent experimental data from the U.S. and Europe that indicate the potential to achieve higher

$SO_2$ removal efficiencies at practical sorbent injection rates, if combustion and sorbent conditions can be properly controlled. New combustion systems being developed to control emissions of nitrogen oxides ($NO_x$) fortuitously may help achieve these necessary conditions. Specifically, controlled mixing conditions associated with low-$NO_x$ combustion may provide new opportunities to optimize the sorbent injection process and also provide the added benefit of simultaneous in-furnace $NO_x$ and $SO_2$ control. A final factor contributing to the resurgence of interest in dry sorbent injection is the growing incentive for low-cost incremental $SO_2$ controls applicable to existing as well as new power plants. Also, the potential exists for combining furnace sorbent injection with other $SO_2$ control technologies. For instance, its use along with coal cleaning or coal blending may provide $SO_2$ emission compliance flexibility or allow purchase of cheaper, higher sulfur coals for existing units. Other opportunities may result from integrating this process with other $SO_2$ flue gas treatment systems, with the possibility of providing overall $SO_2$ control capability adequate to meet higher $SO_2$ control requirements for new plants.

## EPRI RESEARCH RESULTS

To provide a perspective on EPRI's R&D program, Table 1 lists a number of the development issues that ultimately need to be resolved before widespread application of this process can be considered. Regarding the $SO_2$ capture process itself, it is a complex physical/chemical process which is by no means completely understood. There are a multitude of parameters affecting $SO_2$ capture: sorbent properties, coal properties, injection system design, and boiler temperature characteristics just to name a few. A big issue in this regard is how to improve calcium utilization which, in much of the work to date, has been in the 20 to 25 percent range.

Another area requiring further R&D is the impact of the process on the rest of the plant. The introduction of limestone or other alkaline materials into the furnace cavity not only adds to the total mass of solids in the boiler but changes the physical and chemical characteristics of the ash. This in turn can affect: 1) slagging and fouling deposits on the furnace heat transfer surface, 2) convective pass tube erosion, 3) and back end ash deposition patterns. These potential problems can conceivably be designed out of a new unit, but they could be a serious issue especially for retrofits. Another major question concerns the effect on the electrostatic precipitators. Increased ash loading and higher ash resistivity will likely result in degraded ESP performance. This again would be an especially relevant issue for retrofits.

Finally, these development issues and their likely site-specific solution result in a level of uncertainty regarding the cost of commercial application. In addition to the technical development programs at EPRI, an important objective is to provide realistic cost estimates for utility boiler applications and refine these estimates as the development efforts proceed. The following discussion focuses on the results from EPRI projects in the areas of: 1) sulfur removal capability and process development, 2) boiler slagging and fouling consequences and 3) current process cost estimates.

Table 1. Furnace Sorbent Injection Unresolved Commercialization Issues

- INADEQUATE PROCESS UNDERSTANDING FOR OPTIMUM $SO_2$ REMOVAL
- BOILER SLAGGING AND FOULING CONSEQUENCES
- CONVECTIVE PASS EROSION
- AIR HEATER DEPOSITION
- PARTICULATE COLLECTOR PERFORMANCE
- ASH HANDLING AND DISPOSAL REQUIREMENTS
- RETROFIT LOW-$NO_x$ BURNER AVAILABILITY AND NEED
- RETROFIT CAPITAL AND OPERATING COST

PROCESS DEVELOPMENT

To confirm the $SO_2$ removal potential of sorbent injection, pilot testing was performed by Mitsubishi Heavy Industries (MHI) in a jointly sponsored project with the Electric Power Development Company of Japan. (2) These initial proof-of-concept tests were conducted on a 80 million Btu/hr (24 $MW_t$) test furnace equipped with MHI's low-$NO_x$ "PM" burner. An earlier EPRI project with MHI and Combustion Engineering to verify the $NO_x$ control performance of the PM burner (3) established that temperature and combustion conditions in this furnace closely similated those of an actual utility boiler.

The sorbent injection testing was intended to demonstrate $SO_2$ removal without process optimization, and also provide a preliminary indication of the influence of major process and combustion parameters. Two coals selected for the tests were a Japanese high sulfur bituminous coal (3.1% sulfur) and a low-sulfur western U.S. subbituminous coal (0.7% sulfur). A high calcium limestone was used as the sorbent.

Initial screening tests evaluated a variety of sorbent injection locations within the furnace. These included the burner's coal and secondary air nozzles, and separate ports downstream of the burner zone used to inject air (overfire air ports) or recirculated flue gas into the furnace. Injecting the limestone through the overfire air ports was the most effective approach. Typical results on both coals are shown in Figure 1 for a range of limestone injection rates (expressed as Ca/S molar ratio).

For the bituminous coal, $SO_2$ removal was over 40% at a Ca/S of 2 and approached 60% at a Ca/S of 3. This corresponds to a calcium utilization of about 20 percent. The $SO_2$ removals for subbituminous coal were consistently lower at an equivalent Ca/S ratio. Other parameters, including limestone fineness, furnace excess oxygen and coal firing rate influenced $SO_2$ capture but to a lesser extent than sorbent injection location and Ca/S.

To complement the pilot tests, MHI also conducted a series of bench scale experiments to examine $SO_2$ capture under idealized laboratory conditions. These tests used a small flow reactor in which pulverized limestone and synthesized flue gas mixtures could be mixed and reacted. Fundamental parameters such as reaction temperature, sorbent/$SO_2$ contacting time and initial $SO_2$ concentration could be independently varied. An example of the data from this work is shown in Figure 2. The results indicated that there exist optimum combinations of temperatures and reaction times which maximize $SO_2$ capture for a given sorbent material. The highest $SO_2$ removals were observed at the longest reaction time of 1.5 seconds which may not be unlike the residence time typically available in the furnace of a utility boiler. The effects of $SO_2$ concentration observed in the pilot testing were also duplicated in the flow reactor.

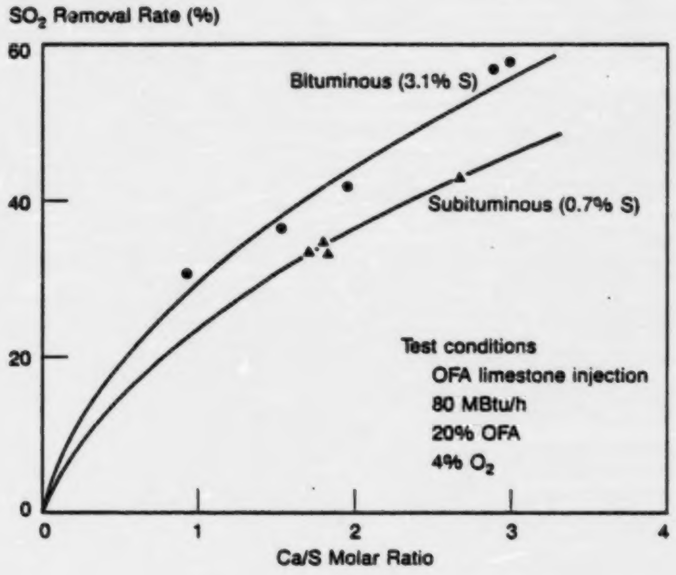

Figure 1. SO$_2$ Removal Efficiency Versus Ca/S -- 80 MBtu/hr Pilot Tests

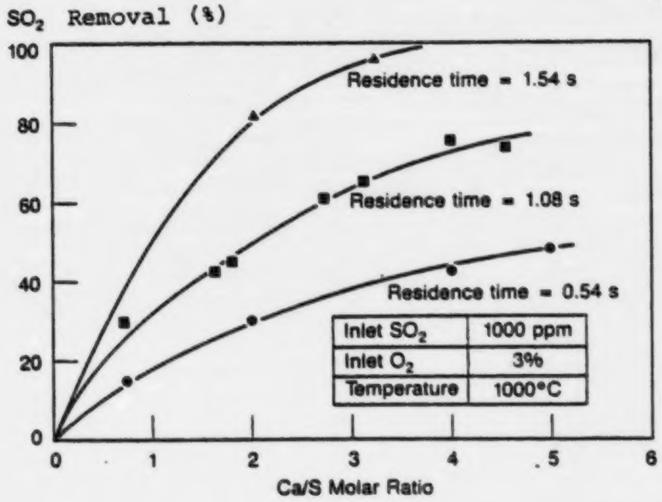

Figure 2. Effect of Residence Time on SO$_2$ Removal Efficiency -- Bench Scale Flow Reactor Tests

The MHI pilot and bench scale work verified the potential for $SO_2$ control and provided some insights into the $SO_2$ removal process. However, these programs along with other research efforts in the U.S. and abroad have also identified major deficiencies in the current understanding of the mechanisms and applicability of the process. For example, serious questions concerning the most effective way to improve calcium utilization, and process design criteria for the range of furnace conditions encountered throughout the utility boiler population, still remain. Such questions need to be resolved before full scale application of the process can proceed.

To complete the process development, a jointly funded project with Southern Company Services has been initiated. This project involves continuation of bench and pilot testing with the objective of developing design guidelines for utility boiler applications. Furnace sorbent injection alone and its integration with dry "back end" flue gas treatment processes, are being considered. Southern Research Institute and KVB, Inc. are subcontractors performing the pilot and bench scale testing. This work is scheduled for completion in early 1985.

## POWER PLANT IMPACTS

As mentioned previously, the introduction of limestone or other sorbents into the furnace will alter the chemical and physical properties of the fly ash as well as increase the quantity of solids passing through the boiler. For example, as shown in Figure 3, a limestone injection rate corresponding to a calcium/sulfur ratio of 2.0 would increase total solids loading 25% for a coal containing 0.5% sulfur and 10% ash, but would nearly tripple the solids for a 4% sulfur, 10% ash coal. (4)

Based on a review of earlier utility experience with this technology, a preliminary retrofit feasibility study by Combustion Engineering identified a number of possible related power plant impacts. (1) Foremost among these are the likelihood for increased slagging and fouling deposits on furnace heat transfer surfaces and degraded electrostatic precipitator performance, in addition to increased ash handling and disposal requirements.

A preliminary indication of potential fouling and slagging consequences was obtained during pilot combustion tests by Combustion Engineering (5). Tests were conducted at CE's 4 MBtu/hr Fireside Performance Test Facility (FPTF) to measure the slagging and fouling properties of fly ash produced during limestone injection. The FPTF similates the: 1) geometry, temperature ranges, and velocities of a utility boiler's convective section, and 2) thermal environment of the radiant furnace walls. Two coals with differing ash characteristics, representing a range of slagging and fouling behavior encountered in the utility industry, were examined. The first coal, a high iron content Midwestern bituminous coal (3.4% sulfur) characteristically exhibits high slagging and moderate fouling tendencies. The second coal, a high sodium content Western subbituminous coal (0.5% sulfur) exhibits high fouling and moderate slagging behavior.

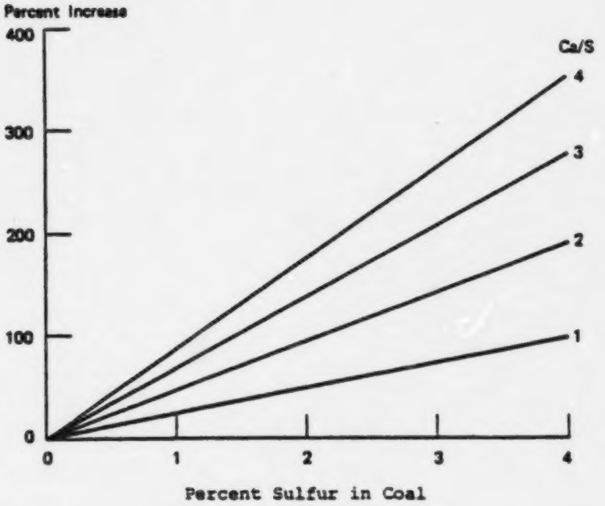

Figure 3. Increased Boiler Solids Loading During Furnace Limestone Injection for 10% Ash Coal

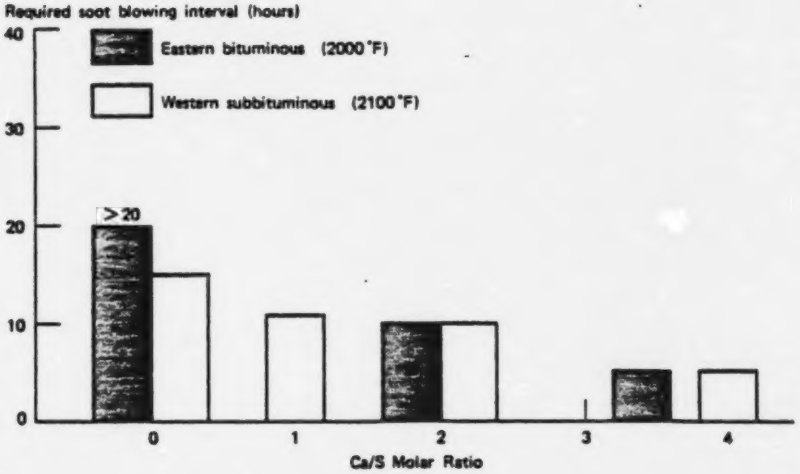

Figure 4. Impact of Furnace Limestone Injection on Convective Pass Sootblowing Frequency (Ca/S = 2)

The focus of the work was on measuring the chemical and physical properties of the deposits including chemical composition, deposit accumulation rate, deposit bonding strength, heat transfer effects, and ease of removal ("deposit cleanability"). These measurements were than utilized by CE to predict the impact of furnace limestone injection on boilers firing these two coal types. For both coals, the increased mass loading during limestone injection resulted in a greater fouling deposit accumulation rate on the convective tubes. However, increased deposit friability and lower deposit-to-tube bonding strength enhanced the effectiveness of conventional sootblowing by improving deposit cleanability. For the Western subbituminous coal, the addition of limestone may serve to alleviate severe fouling problems commonly encountered with this type of coal. Generally, it appears that the increased fouling deposit accumulation rates with limestone addition can be managed with conventional sootblowing equipment, although increased sootblower frequency (Figure 4) and/or additional sootblowers are likely to be required.

Limestone injection also increased the quantity of slagging deposits in the radiant section. The physical characteristics of the deposits were also affected. In general, the addition of limestone resulted in a drier, more friable deposit which is more easily removed with conventional sootblowing. To overcome the increased quantity of slagging deposits more frequent sootblowing would be required.

One significant result of the FPTF work was to demonstrate a laboratory procedure to determine the slagging and fouling consequences of furnace limestone injection. While the results obtained pertaining to these two coals were instructive in developing the general impact of limestone injection on boiler heat transfer surfaces, utility companies considering this technology for retrofit would be advised to consider similar tests to screen particular coals for their slagging and fouling characteristics due to the variability in coal properties. Engineering studies would also be necessary to account for unit-specific factors such as furnace design, convective tube spacing and geometries, sootblower coverage and ash handling capabilities.

## ECONOMICS

The capital and operating costs of furnace limestone injection have been estimated by Combustion Engineering (1), Stearns-Roger (6) and KVB (4) for new and retrofit applications. For new 500 MW boilers equipped with fabric filter particulate controls, the incremental capital cost estimates range from \$15 to 30/kW depending on coal sulfur content and the Ca/S ratio (1,6). The major portion of these costs are associated with limestone delivery, storage, pulverization and injection (including combustion system design modifications) which represent added plant components not otherwise needed.

For retrofit applications (1,4) the capital cost can be considerably higher due to the probable need for upgrading sootblowing systems, electrostatic precipitators and ash handling and disposal systems. Such costs would be very site specific but could result to total retrofit capital costs 2 to 3 times the new unit costs. The range of capital cost estimates associated with the major plant subsystems affected are shown in Figure 5. The total plant incremental capital costs for two retrofit scenarios are summarized in Figure 6.

The operating costs increase nearly proportionately to coal sulfur content. This reflects the fact that higher coal sulfur requires greater quantities of raw sorbent and produces more byproduct for disposal, both of which represent major operating cost items. As shown in Figure 7 for Ca/S ratios between 2 and 3, 30-year levelized operating costs range from about 3 to 5 mills/kW-hr for a 0.5% sulfur coal and increase to 8 to 12 mills/kW-hr for a 4.0% sulfur coal. As additional research further defines the process design and plant upgrading requirements, refinements in these preliminary cost estimates will be possible.

## FUTURE RESEARCH

In addition to the research described above, results from other EPRI projects are expected to be applied to this technology. Low-$NO_x$ burner evaluations (7) with Riley Stoker, Babcock & Wilcox, Combustion Engineering, MHI and KVB, Inc. are aimed at demonstrating retrofit $NO_x$ combustion control systems and providing the guidelines for their application. If such systems are shown to be an essential element of the sorbent injection process, the results from these efforts would play a key role in its commercial application. In addition, research by Southern Research Institute on flue gas conditioning and pulsed energization (8) for enhancing electrostatic precipitator performance could play an important part where the retrofit application of furnace sorbent injection may require upgrading of existing particulate controls.

These efforts together with the process development, boiler impact studies and economic evaluations discussed above will provide the groundwork for prototype testing of sorbent injection of coal utility boilers. The retrofit of several boilers in the 40 to 100 $MW_e$ size range is considered the next logical step towards determining the commercial potential of this process. They will enable final optimization and verification of the sorbent injection process design and also allow economical resolution of remaining plant impact issues that may not be fully accomplished in laboratory tests. Experimental work at the prototype scale will include evaluation of 1) alternate electrostatic precipitator upgrades, 2) long term effects on furnace slagging, fouling and erosion, 3) alternate sorbent injection systems, and 4) ash handling and disposal requirements.

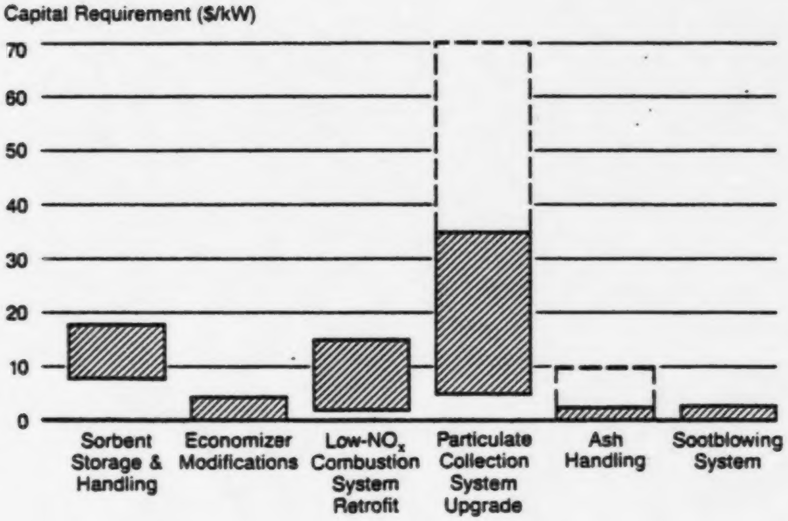

Figure 5. Range of Power Plant Subsystem Capital Costs for Retrofit Furnace Limestone Injection. Particulate Control Costs Correspond to: Fly Ash Conditioning ($5/kW), Double SCA ($35/kW) and Baghouse Retrofit ($70/kW)

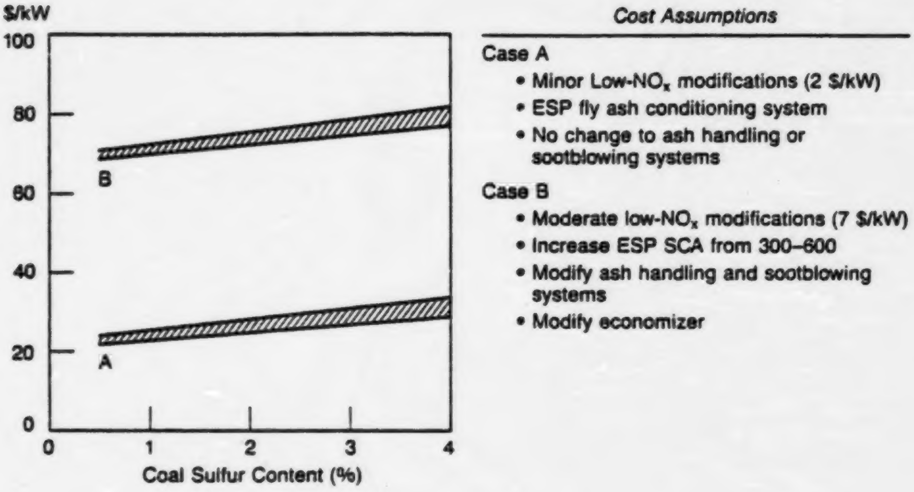

Figure 6. Estimated Capital Requirement of Furnace Limestone Injection

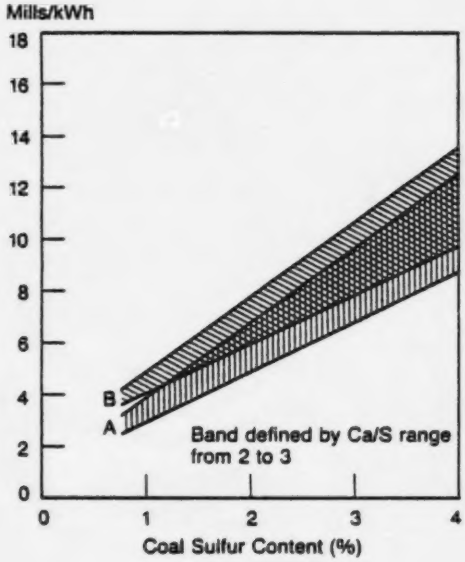

Figure 7. Estimated 30-Year Levelized Busbar Costs of Furnace Limestone Injection (Cases A and B same as Figure 6)

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# DIRECT DESULFURIZATION THROUGH ADDITIVE INJECTION IN THE VICINITY OF THE FLAME

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## ABSTRACT

After a short description of the staged mixing burner, the report goes on to deal with the process of direct desulfurization in the furnace of steam generator by injection of additives around the flame. Further, the results from tests with a pilot burner and intermediate results from tests in a full-size boiler are given. Finally, the possible applications and economic aspects of direct desulfurization are discussed.

Direct desulfurization is defined as binding of sulfur within the boiler itself (Figure 1).

- Fluidized-bed firing: A well-known process is fluidized-bed firing, which is not the subject of this paper.
- Flame firing: We want to take a look at direct desulfurization in flame firing, which is basically not a new system at all. Beginning as long ago as the early fifties, people have tried for various reasons to bind sulfur by injection of calcium-containing additives. In the early sixties, the idea behind this was to prevent corrosion ($SO_3$ binding) but lately the emphasis has shifted to reduction of noxious emission ($SO_2$ binding), which remains the main concern today.

  These investigations have revealed that certain quite definite conditions must be fulfilled for reaction temperature and residence time if the desulfurization process is to proceed.

  1. Additive injection above flame zone: The idea of injecting the additive above the flame zone is to try to avoid the sintering of the active surface area of the additive which occurs at too high a temperature. The disadvantage of this process is the greatly inferior mixing of the reactants just at the point where the temperature is most favorable for the desired reaction.

a) Fluidized - Bed Combustion

b) Flame Firing

- Additive injection above the flame zone
- Additive mixed with the fuel
- Additive injection around the flame

Steinmüller-Direct Desulfurization Process "DEP"

| | | |
|---|---|---|
| STEINMÜLLER | DIRECT DESULFURIZATION<br>(Desulfurization in Boiler) | Fig. 1 |

2. Addition of additive to the fuel: If the additives are introduced with the fuel, they inevitably pass through the region of highest flame temperatures. Processes of this kind are therefore restricted to use with fuels of low calorific value, i.e. with relatively low flame temperatures.

   It can therefore be readily understood that in bituminous coal-firing systems, desulfurization results are much less satisfactory than with lignite coal-firing systems.

3. Additive injection around the flame: The rest of this paper will deal with additive injection around the flame.

In this process, which is still in the development stage, all necessary conditions for sulfur binding within the boiler in respect to temperature, mixing and residence time can be more effectively fulfilled, even for high calorific value coals and at a reasonable cost.

Before we go on to discuss the technical details of this process, we should like to touch briefly on the physical fundamentals of the direct desulfurization reaction.

When $Ca(OH)_2$ or $CaCO_3$ are employed as additives to capture $SO_2$ and other pollutants, the dehydration or decarbonation (calcination) of the additives takes place according to reactions (1) and (2) (Figure 2).

$$Ca(OH)_2 \rightarrow CaO + H_2O \qquad (1)$$

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (2)$$

The heterogeneous gas/solid reactions which occur during capture of pollutants in the furnace and downstream of it take place under a constant overall pressure which lies just below that of atmospheric pressure. Pollutant reactions (3) to (6) can be expected to occur.

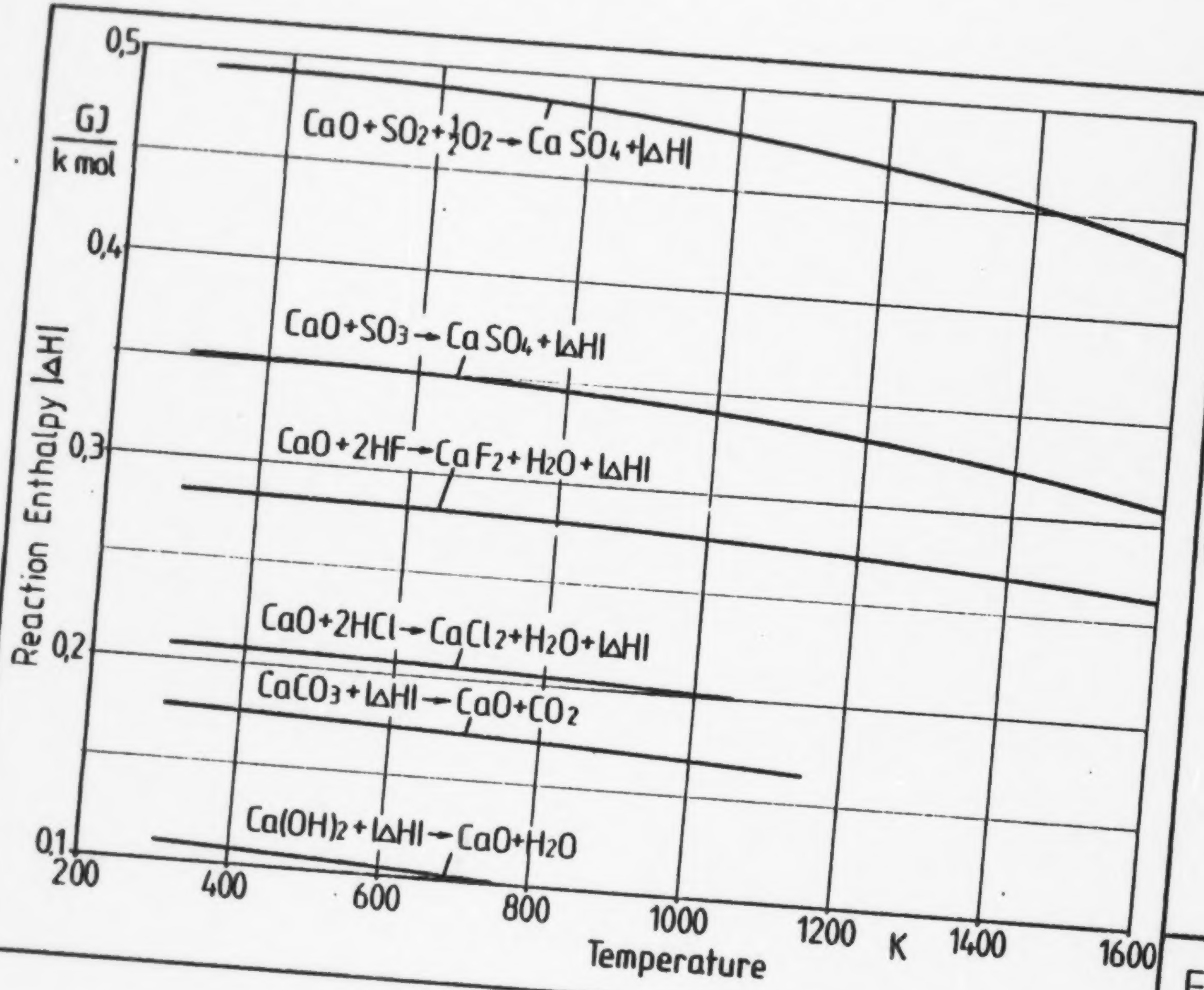
$$CaO + SO_2 + 1/2O_2 \rightarrow CaSO_4 \qquad (3)$$

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O \qquad (4)$$

$$CaO + 2HF \rightarrow CaF_2 + H_2O \qquad (5)$$

$$CaO + SO_3 \rightarrow CaSO_4 \qquad (6)$$

The enthalpies of reactions indicate that dehydration and decarbonation are endothermic and all pollutant capture reactions exothermic. In Figure 2 the development of the reaction enthalpies for reactions (1) to (6) is shown as a function of temperature. If the thermal energy required for the formation of CaO is now compared with that liberated as a result of sulfation, we find that, for full recovery of the dehydration/decarbonation energy, a calcium efficiency of 22% or 36%, respectively, is required. Calcium efficiency is the term used to describe the percentage of injected calcium utilized for stoichiometric binding of the $SO_2$.



Reaction
Enthalpy
as a function of
temperature

Fig. 2

Figure 3 shows the equilibrium curves for the dehydration and decarbonation reactions. Since these two reactions do not tend of their own volition, the reaction temperature must lie higher than the equilibrium temperature. Assuming a portion of 5% $H_2O$ and 15% $CO_2$ in the flue gas, dehydration will take place at temperatures above 385°C and decarbonation at temperatures above 760°C.

In Figure 4 the $SO_2$ partial pressure is presented as a function of temperature for $O_2$ contents in the flue gas of 1% and 6%, respectively. Using these equilibrium curves, it is possible, for a given $SO_2$ partial pressure, to make an initial prediction on the possibility of stable sulfur dioxide binding at the flue gas temperatures obtaining in the furnace. Sulfur capture is possible when the temperature falls below the equilibrium temperature predicted by the equilibrium curve for a given partial pressure of sulfur dioxide. At an overall pressure of 1 bar and 6% excess oxygen in the flue gas, the equilibrium temperature for an $SO_2$ concentration of 800 ppm is approximately 1160°C.

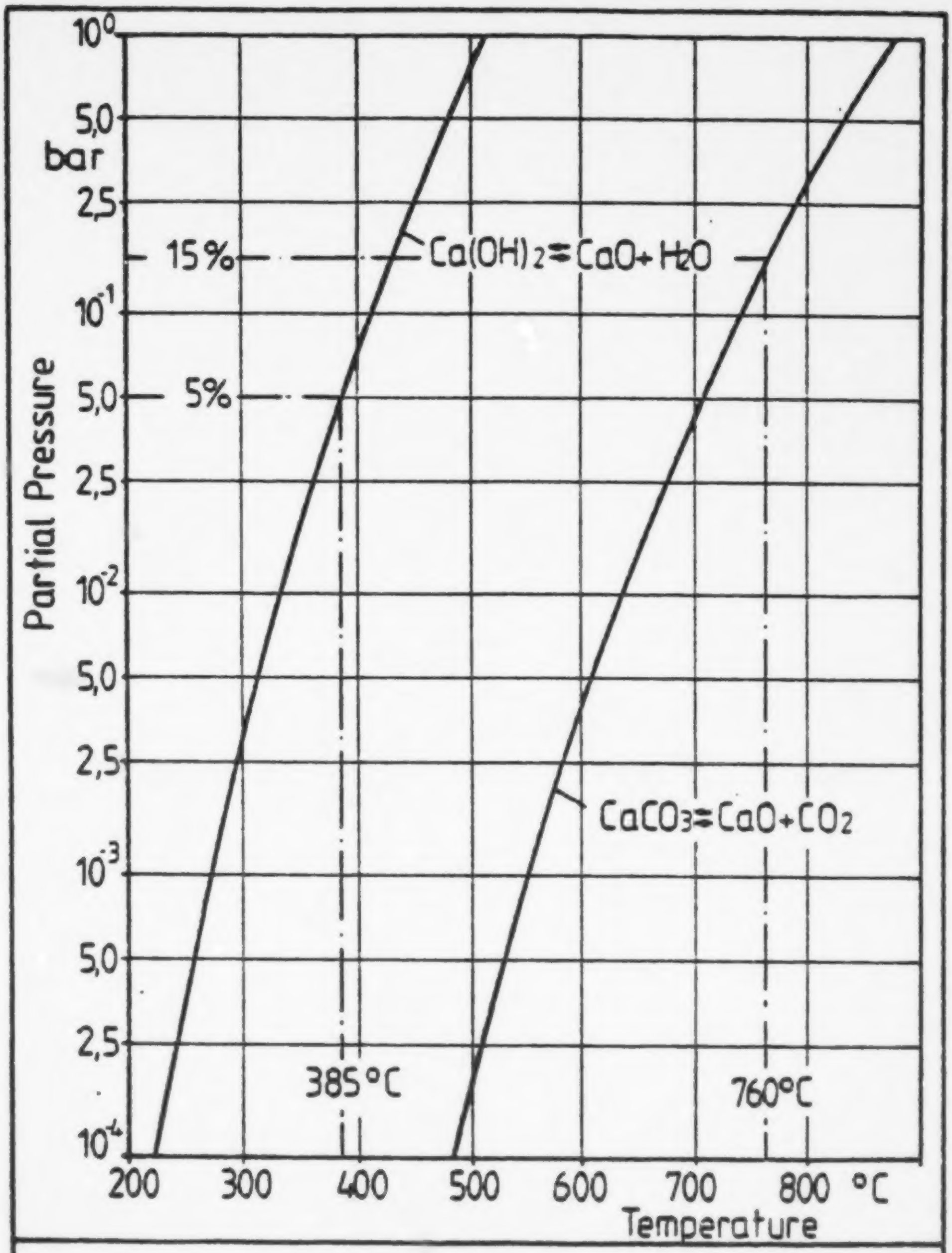
These considerations based on chemical thermodynamics show that, providing additive and flue gases are thoroughly mixed and no sintering of the particle surface takes place, desulfurization of the flue gases in the boiler is possible. The question whether a reaction which is theoretically possible on thermodynamic grounds will actually take place at the required speed is one of reaction kinetics and cannot therefore be answered on the basis of equilibrium considerations.

Very few data are available on the reactions here described (Figure 5). In the sixties, Wickert carried out laboratory experiments to determine the effect of temperature upon desulfurization efficiency and his results are presented here. It can be seen that $Ca(OH)_2$ as an additive is significantly more effective than CaO and demonstrates maximum sulfur capture efficiency in the temperature range from 800°C - 1000°C.

These theoretical considerations show that direct desulfurization would also seem to be possible in the furnace of flame-firing systems when the additive is injected around the burner. An integral component of this process is the staged mixing burner which has been developed in the last few years for the purposes of low $NO_x$ combustion. Its working principles are outlined in Figure 6.

The design of the staged mixing burner is based on the reliable circular-type burner, which has enjoyed an excellent track record over many years. In this burner the p.f./air mixture is introduced into the furnace via an annular section.

In the staged mixing (SM) burner, the secondary air is divided into a secondary air flow proper and a staging air flow. The secondary air enters the furnace via an annular nozzle concentric with the p.f./air nozzle. Interaction between the p.f./air mixture and the secondary air flow produces a primary combustion zone in the area of the burner throat where substoichiometric conditions reign.



pt-Diagram

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Fig. 3

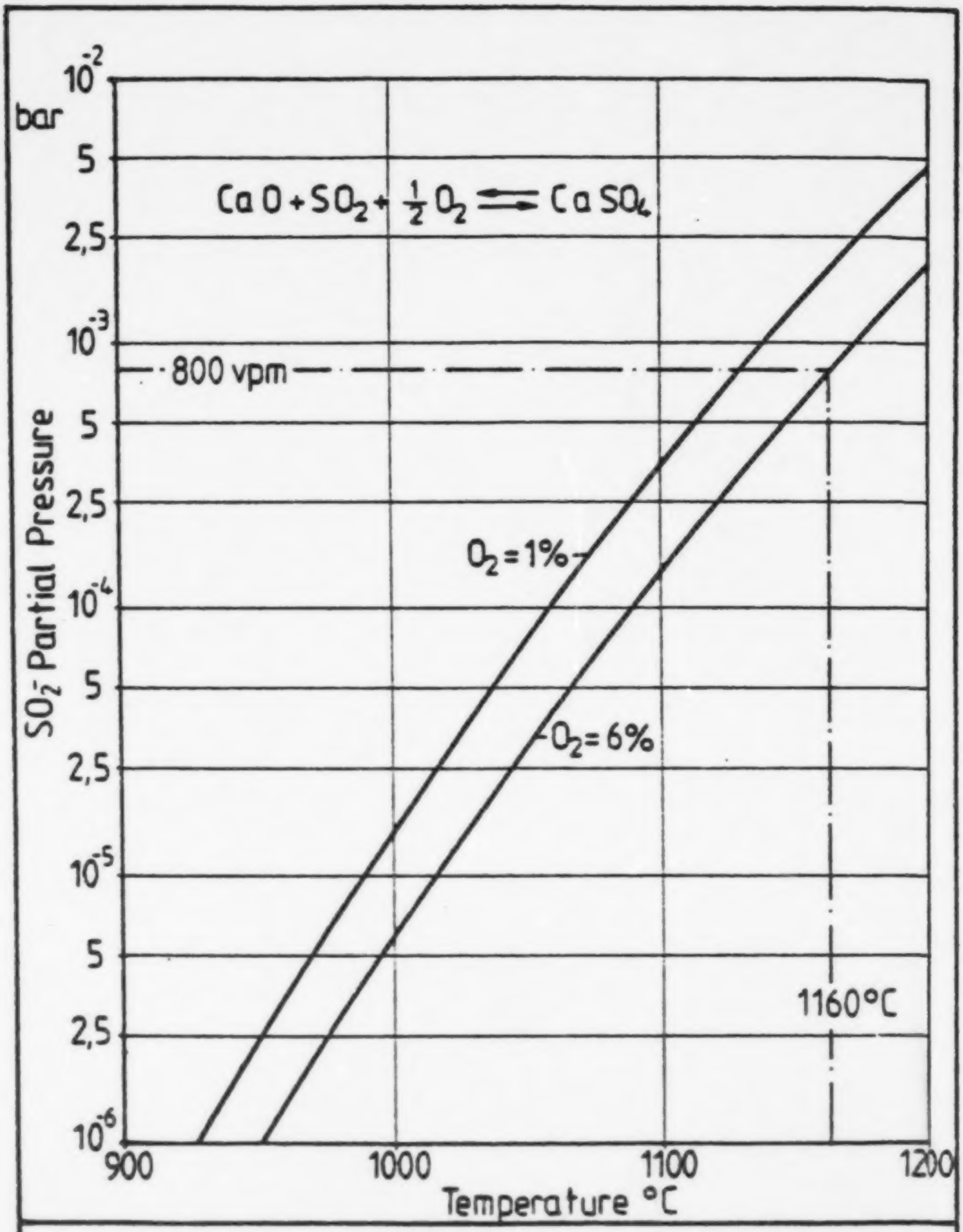

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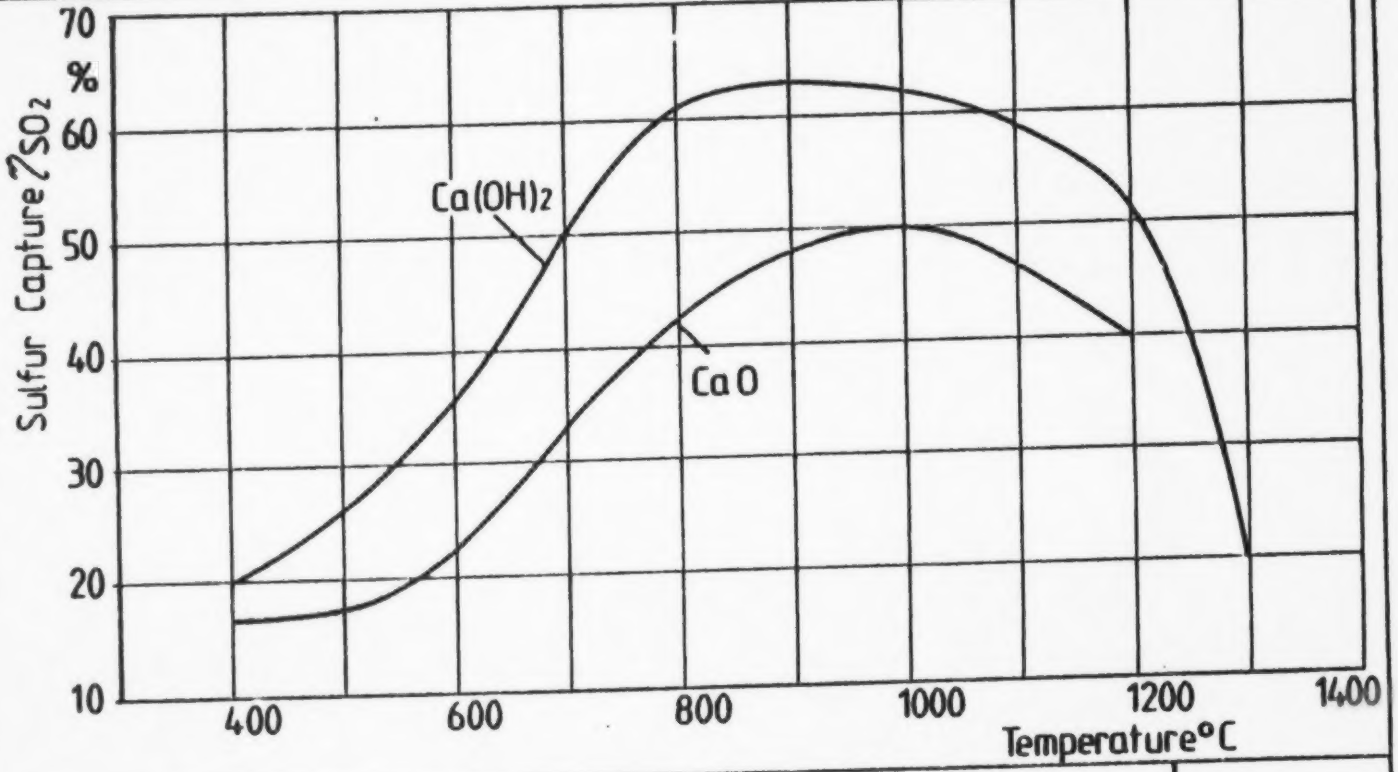
Fig. 4



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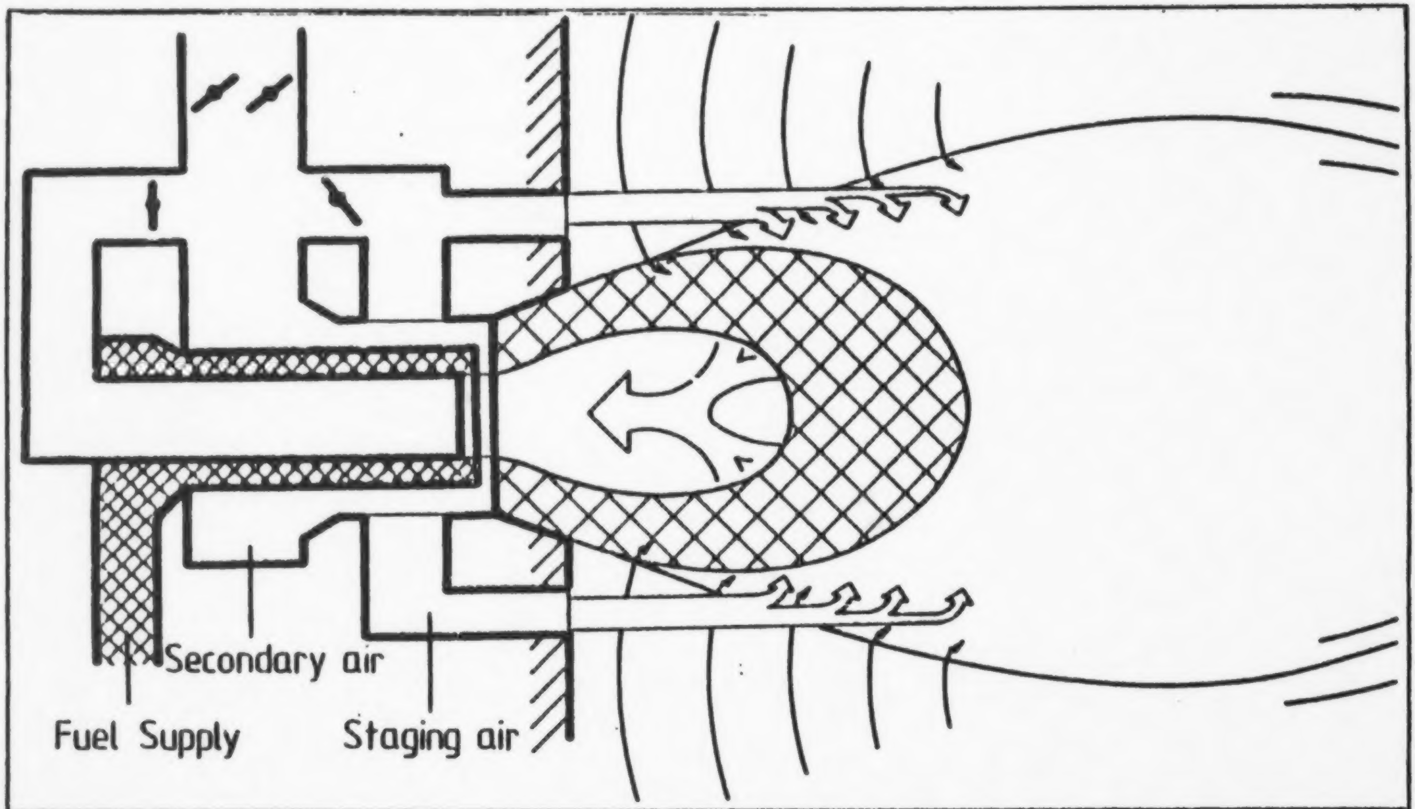
Influence of Temperature
on Sulfur Capture

Fig.5



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SM Burner Flow Pattern

Fig. 6

To ensure full combustion the staging air is nozzled in around the primary flame into the burnout zone in a number of individual streams.

As has already been reported, this SM burner is capable of reducing $NO_x$ formation (and therefore pollutant emission) by more than 50%.

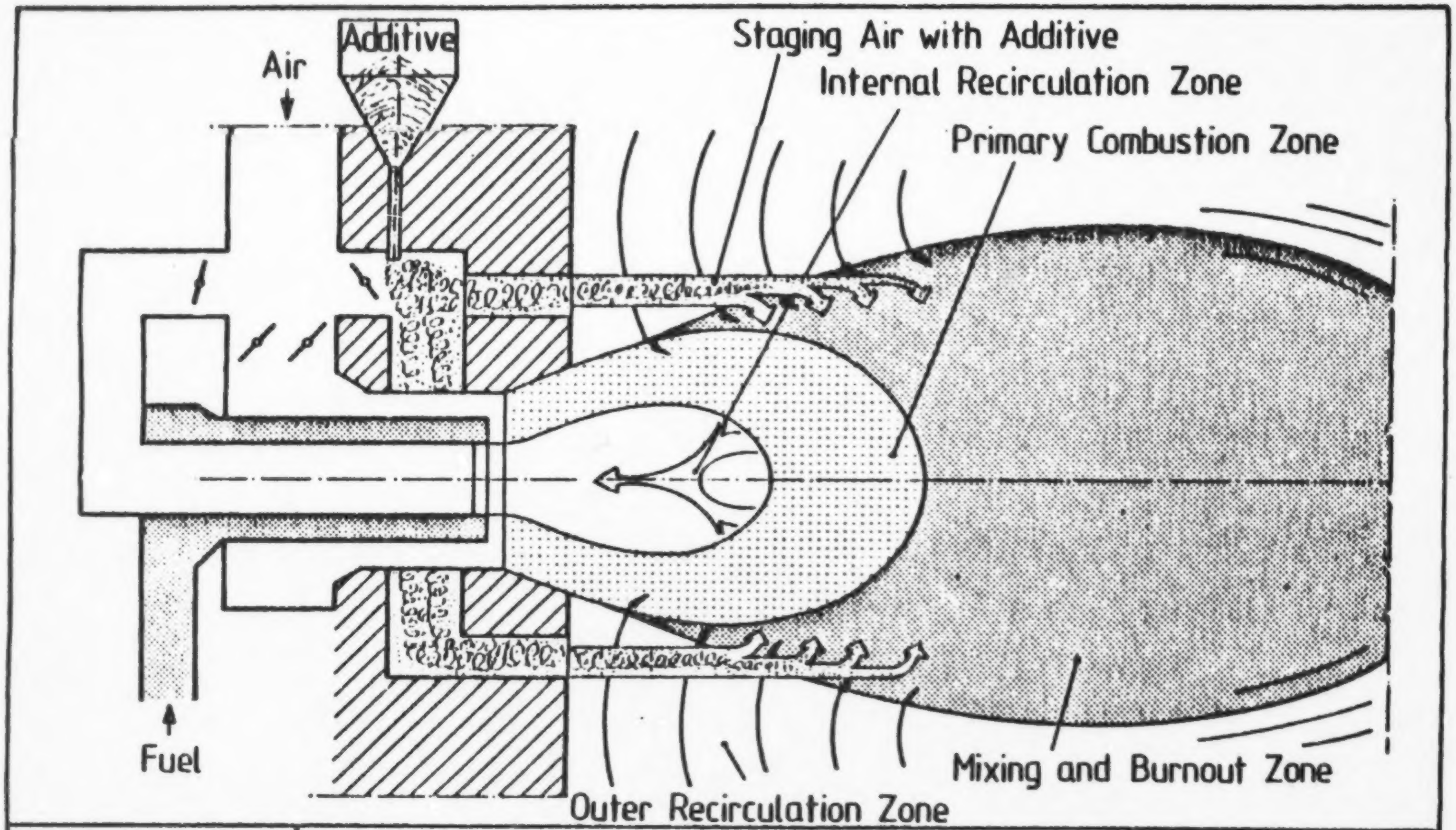
Compared with earlier circular-type burners, the SM burner offers improved possibilities for injecting the additive into the furnace in such a way that the three essential conditions for sulfur capture, viz, temperature, mixing and residence time, can be realized (Figure 7). For the most part, the additive does not enter that area of the flame where the highest temperatures are found and thus sintering of the additive surface can be avoided. The high turbulence around the flame ensures excellent mixing of the additive with the flue gases. Practically the same maximum residence time from burner to electrostatic precipitator is available for sulfur capture as with additive injection mixed with the fuel, but the disadvantages of the latter method are avoided.

To discover the attainable sulfur capture levels and optimize the process, Steinmüller has carried out experiments at the International Flame Research Foundation (IFRF). The most important results obtained are listed below.

The following relevant parameters were examined (Figure 8):

- Fuel: Natural gas doped with $SO_2$ or $H_2S$ and three different types of bituminous coal.
- Additive: $Ca(OH)_2$, $CaCO_3$ and activated $Ca(OH)_2$.
- Molar ratio Ca/S: From 1 to 4.
- Point of additive injection on burner: With staging air, with fuel and via nozzles in the external recirculation zone (ERZ).
- Partial air flow rates at burner: Ratios of air (n) and air in the primary combustion zone ($n_p$ from 0.6 to n).
- Flue gas temperature: From 900°C to 1100°C.
- Swirl: From minimum to maximum.
- Load: From 60% to 150%.
- Velocity of staging air: Low and high.

Figure 9 shows the influence of the type of additive, the point of additive injection and the sulfur content in the fuel on the degree of desulfurization as a function of the molar ratio Ca/S.



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Direct Desulfurization through Additive Injection around the SM Burner

Fig.7

Fuel
Natural gas doped with $SO_2$, 3different bituminous coals, Heavy Fuel Oil

Additive
$Ca(OH)_2$, $CaCO_3$, $Ca(OH)_2$ -active

Molar Ratio Ca/S
from 1 to 4

Additive injection location on burner
Staging air, fuel, tubes in ERZ

Airflow ratios at burner
n,np = 0,6 to n

Furnace Temperature
from 900°C to 1100°C

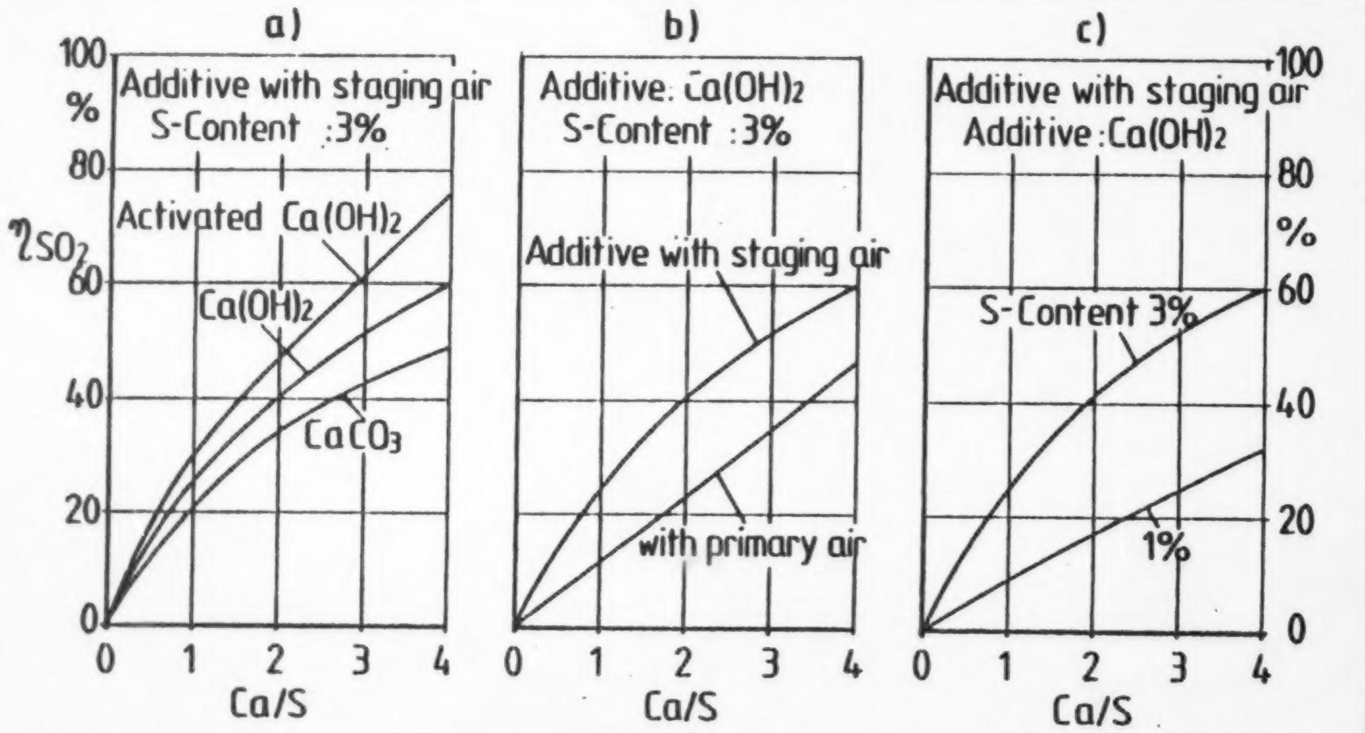
Swirl
from minimum to maximum

Load
from 60% to 150%

Velocity of staging air
low, high

Parameters tested at IFRF/Ijmuiden

**STEINMÜLLER** Fig. 8



STEINMÜLLER

Sulfur capture $\eta_{SO_2}$ as a function of molar ratio Ca/S with natural gas

Fig.9

The type of additive has a very definite influence on sulfur capture. $CaCO_3$ has a lower affinity for sulfur than $Ca(OH)_2$. Activated $Ca(OH)_2$ by contrast only demonstrated better desulfurization potential when the $SO_2$ concentration in the flue gas was high. Activated calcium hydroxide is manufactured by grinding quicklime with fatty acids and then slaking with a calcium chloride solution, so that the finished product contains around 2% $CaCl_2$.

This figure shows the influence of the point of additive injection on the degree of desulfurization. Injection into the flame core produces significantly worse desulfurization than when the additive is injected into the outer recirculation zone of the flame, e.g., with the staging air. This tendency is to lower sulfur capture when $Ca(OH)_2$ is injected with the transport air can be attributed to the longer residence time of the additive particles in the hot flame zone. As a result, the activity of the additive is considerably reduced by sintering of the surface and the formation of thermodynamically stable $CaSO_4$ prevented.

Sulfur capture is more effective for high sulfur contents in the fuel, at least up to a certain concentration of $SO_2$. This can largely be explained, as can be seen from the pT diagram for sulfation, by the higher dissociation temperature of $CaSO_4$.

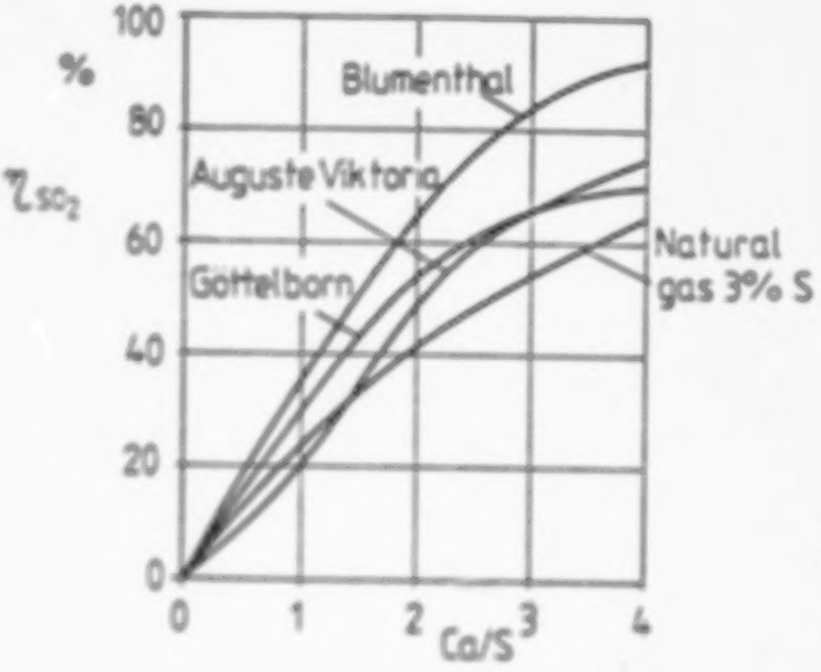
The greater degree of $SO_2$ diffusion towards the additive surface also plays a role.

It can be seen from these diagrams that the levels of desulfurization achieved with doped natural gas were unsatisfactory, both from a technical and an economic viewpoint. Continuation of the experiments with bituminous coals seemed nevertheless justified for two reasons: First of all, earlier tests with coal showed better sulfur capture results even when the additive was injected with the primary air; and, secondly, we achieved an improvement of sulfur capture by injecting additive with the staging air.

The results in Figure 10 show that this conclusion was fully justified. Here the maximum degree of desulfurization measured with various different fuels is presented as a function of the molar ratio Ca/S, using $Ca(OH)_2$ as additive.

Injective of the additive was carried out in the outer recirculation zone of the flame. For Ca/S = 2, the following desulfurization levels were measured:

- 50% for Ruhr coal from the Auguste Viktoria pit with a maximum $SO_2$ concentration in the raw gas of 2385 $mg/m^3$ (SPT dry).
- 57% for Saar coal from the Göttelborn pit with a maximum $SO_2$ concentration in the raw gas of 1810 $mg/m^3$ (STP dry).
- 65% for Ruhr coal from the Blumenthal pit with a maximum $SO_2$ concentration in the raw gas of 7712 $mg/m^3$ (STP dry).



| Fuel | $SO_2$ Concentration in flue gas mg/m³ (STP dry) |
|---|---|
| Blumenthal | 7712 |
| Auguste Viktoria | 2385 |
| Göttelborn | 1810 |
| Natural gas (3% S) | 4693 |

Sulfur capture $\eta_{SO_2}$ as a function of the molar ratio Ca/S

Fig 10

- As a comparison, 41% for natural gas with an $SO_2$ concentration of 4693 mg/m$^3$ (STP dry).

These results show that for coal firing systems, $SO_2$ capture achieves levels at which it becomes a thoroughly realistic prospect in process terms. One of the chief reasons for this shift is the different temperature/time history of the additives in coal-firing systems, as shown by the detailed measurements. On the basis of the pilot experiments we carried out an economic feasibility calculation to see if further development of the process was justified.

The desulfurization costs for a 700 $MW_{el}$ power station were worked out using the direct desulfurization process (Figure 11). These costs were compared with those for a "wet" system flue gas desulfurization plant (FGD) with gypsum as the end product.

The following design data were utilized for the projecting of each plant:

Fuel: Bituminous coal
Sulphur content 1%
Ash 7%

Flue gas: $SO_2$ concentration 2200 mg/m$^3$ (STP dry)

Clean gas: Desulfurization efficiency 72%
$SO_2$ concentration 616 mg/m$^3$ (STP dry)
For FGD 80% of the gas flow is treated with a desulfurization efficiency of 90%.

Additive: For DEP: $Ca(OH)_2$
Molar ratio Ca/S = 4

For FGD: $CaCO_3$
Molar ratio Ca/S = 1.05

The total costs are made up of investment and running costs. Plant costs for DEP are mainly incurred for the additive dosing system (bunker, fan, dosing equipment, pipework, control system, etc.), the increased number of sootblowers and the expansion of the electrostatic precipitator and de-ashing systems, etc. FGD personnel costs are 3:1 by comparison with DEP, although this naturally depends on the degree of automation of the FGD system.

In calculating the investment costs per year, assuming a basic interest rate of 8% per year for the investment capital and an amortization period of 15 years, a redemption factor of 11.7% was calculated.

In addition to the redemption factor, which allows for the annual depreciation and payment of interest on the plant capital, 10% of plant

Fuel: Bituminous coal
S-content 1%
Ash 7%

Flue gas: $SO_2$ 2200 mg/m³ (STP dry)

Clean gas: $\eta_{SO_2}$ 72%
$SO_2$ 616 mg/m³
FGD: 80% of flue gas
with $\eta_{SO_2} = 90\%$

Additive: For DEP: $Ca(OH)_2$; Ca/S = 4
For FGD: $CaCO_3$; Ca/S = 1,05

Total Costs: Investment + Operation

Investment Costs: Additive dosing system, Increased number of sootblowers, Increase in size of ESP and deashing system.
Interest rate: 8%; Amortisation period: 15 years
→ Redemption factor: 11,7% + 10% for taxes Administration and repairs.

Operating Costs: Additive, solid effluents disposal, sootblowing and electric power

## Boundary Conditions for Economic Analysis

STEINMÜLLER Fig. 11

capital was reckoned to be devoted to administration, repairs and taxes, so that the investment costs per year amount to 21.7% of the plant capital investment.

For DEP the operating costs make up the major proportion of the expense, consisting chiefly of those for additive, disposal, cleaning the heating surfaces and power. As far as disposal is concerned, it is assumed that fly ash would have been dumped even without direct desulfurization.

Operating costs are some 50% higher than for FGD but the plant costs are only about 10% of those for the latter.

Figure 12 shows the percentage reduction of desulfurization costs when using DEP instead of FGD with gypsum as the end product, given the boundary conditions which have been assumed.

The reduction in costs is entered for full load, depending on the number of operating hours per year. Because of the high investment costs associated with FGD, this example shows that the smaller the number of operating hours per year, the more significant is the cost saving to be obtained using DEP. For a power station operating 4000 h/annum, the reduction in costs according to this calculation would be 30%.

The economic advantages with DEP increase as the sulfur content of the coal and the size of the plant decrease. This process would seem to be of particular interest for older power stations, where for reasons of space, it is impossible to install FGD equipment but where, in most cases, it is relatively easy to reequip the plants for DEP. Keeping even lower pollutant limits would seem to make a coupling of the two systems--DEP and FGD--desirable, but this problem must be the subject of a separate approach.

After the successful conclusion of the pilot experiments and investigation of the economic viability, it was decided, as the next stage of progress towards commercial application, to confirm the results obtained from the pilot experiments on a full-size steam generator and demonstrate the functional effectiveness of the process. See Figure 13.

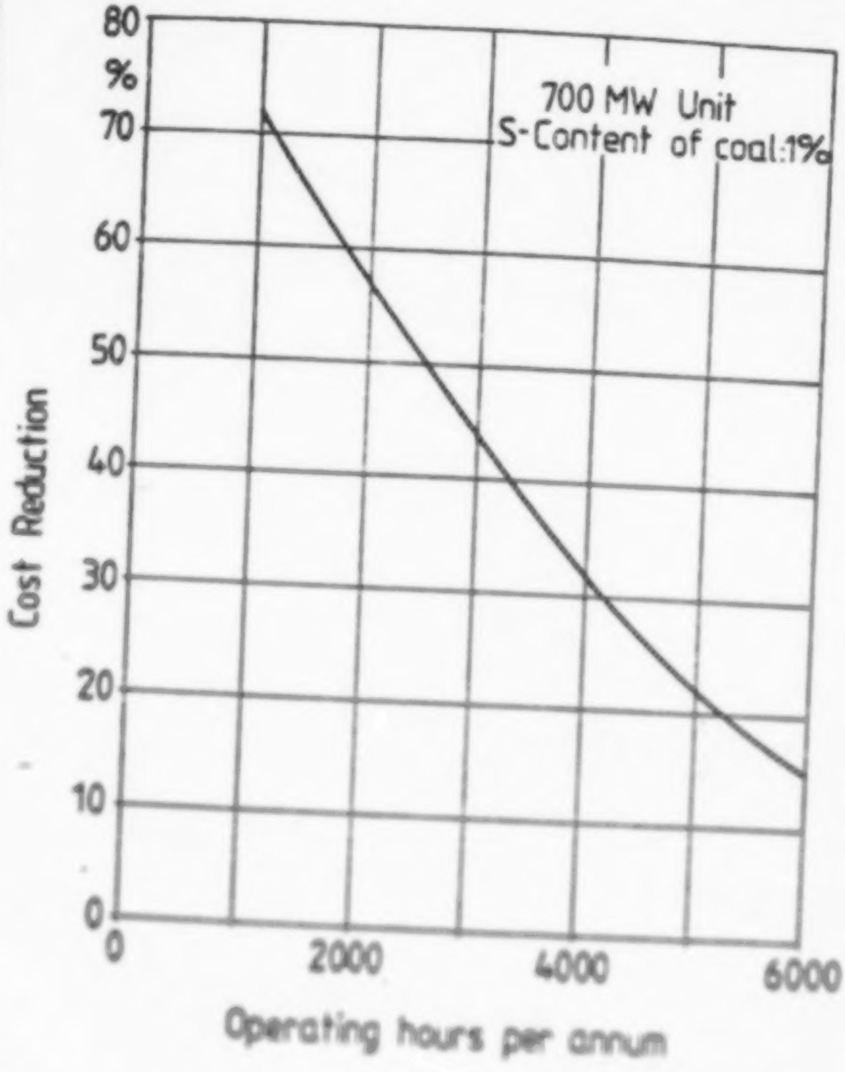
This full-scale technical demonstration will concentrate primarily on the investigation of the following points:

a. Fouling behavior of the boiler furnace.

b. Fouling of the convective banks.

c. Alteration in the ash and its utilization potential.

d. Fouling of the regenerative air heater.



Cost reduction when applying Direct Desulfurization instead of wet FGD

**STEINMÜLLER**

Fig.12

Further investigations using a complete boiler will be carried out to confirm the results so for obtained and explore the following fields:

- Efficiency of desulfurization with multi-burner combustion
- Slagging and fouling behaviour of the boiler
- Possibilities for ash utilization
- Efficiency of the Precipitator
- Scaling and fouling behaviour of the air heater

## Further Work

STEINMÜLLER

Fig.13

e. Dust-collecting efficiency of the electrostatic precipitator.

f. Degree of desulfurization and calcium utilization.

For the investigation of the above points, the Saarbergwerke AG have kindly placed the 700 $MW_{el}$ power station Weiher III at our disposal.

Because of the already installed staged mixing burners, Weiher III is extremely suitable for demonstrating direct desulfurization and $NO_x$ reduction with comparatively little modification.

Figure 14 shows the schematic diagram of the dosing system for the Steinmüller Direct Desulfurization Process applied to Weiher III The furnace of this boiler is divided by a division wall into two combustion chambers and has a total of 24 staged mixing burners, 12 each in the front and rear walls. The 12 burners in these walls are arranged in 3 planes.

Groups of 4 burners are each served by one mill and are supplid with additive by a dosing unit. The additive is transported by the compressed air.

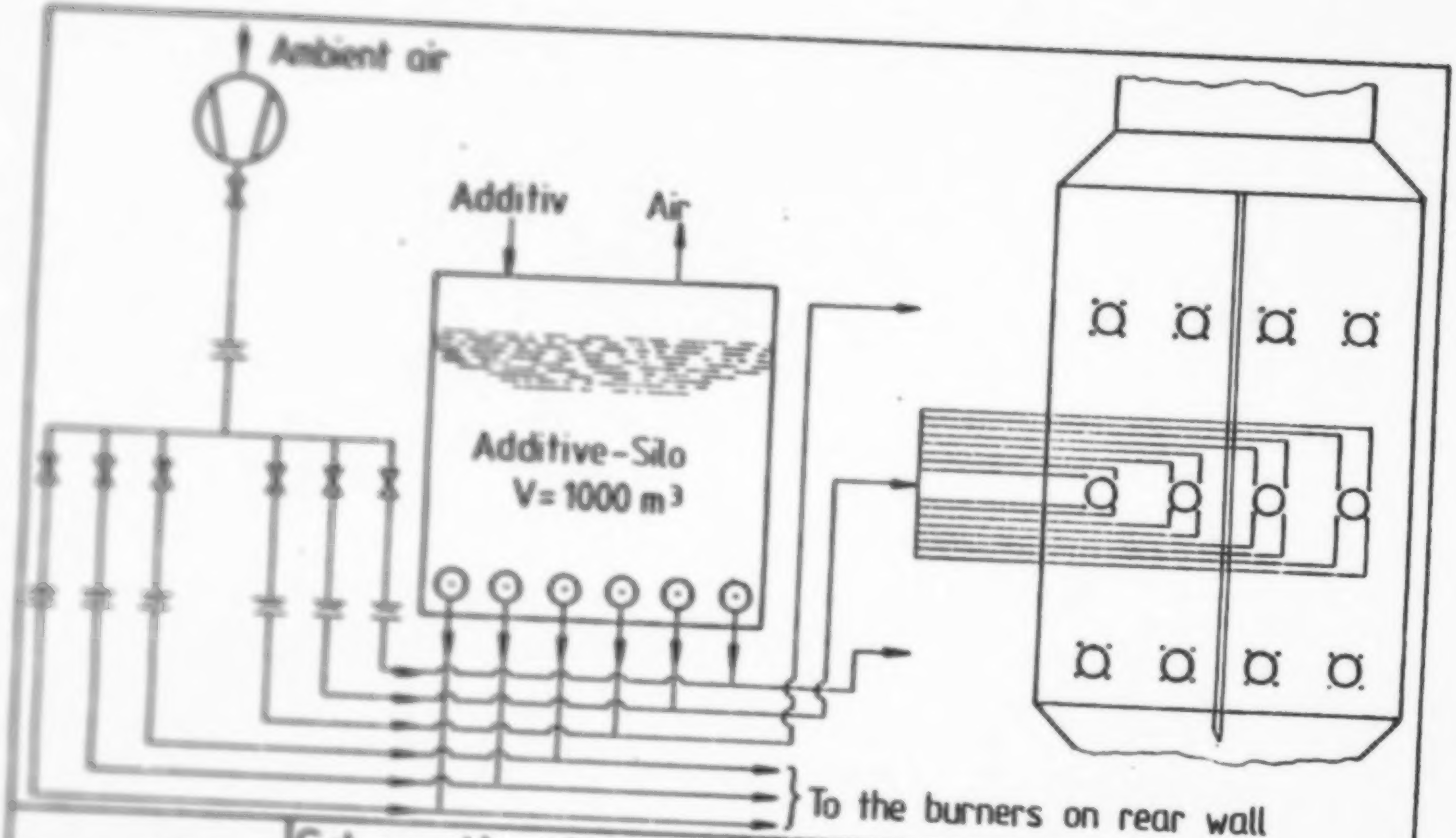
Since availability of the boiler is not to be put at risk in any way, initially only two burners on the middle plane of the left combustion chamber were modified to investigate the potential operating prolems. The object of this first phase was primarily to investigate fouling in the immediate area of the burner, in the furnace and in the convective section, as well as the alteration in the ash. This phase has meanwhile been completed with thoroughly satisfactory results, although there are naturally still points which remain open.

In the following sections the relevant results are presented.

Figure 15 shows the rear wall of the left combustion chamber. Limestone was blown in round the two burners of the centre plane. The view remained the same after the experiments as well, i.e., there were no signs of an increase in fouling and slagging.

The furnace was completely inspected and showed no increase in slagging. Figure 16 shows slagging on the furnace tubes. On the left is the left-hand side wall of the combustion chamber with limestone injection and on the right-hand side wall of the combustion chamber without limestone injection. On both photographs light hard deposits of roughly similar thickness on the side exposed to the flue gas flow can be seen.

Figure 17 shows the first convective heating surfaces after the furnace. A comparison shows that the tubes on the left-hand side of the furnace, where the additive was blown in, exhibit more fouling. But this fouling only appeared in the initial bank and was of a consistency easily dealt with by appropriate soot blowing measures. During the experiments, a total of 300t of slaked lime and 60t of powdered limestone were injected. The experiments continued for four weeks in all.



Schematic of Additive Dosing System for Steinmüller Direct Desulfurization frocess "DEP"

Fig. 14

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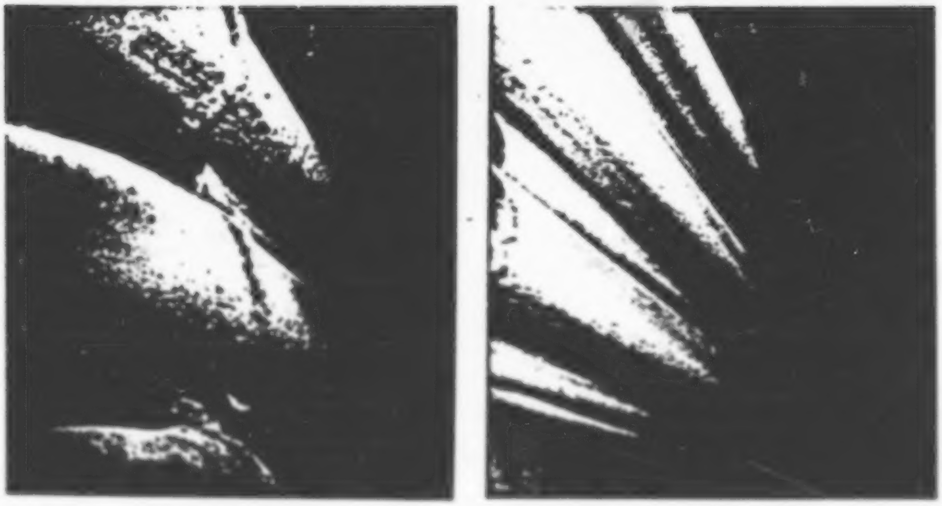
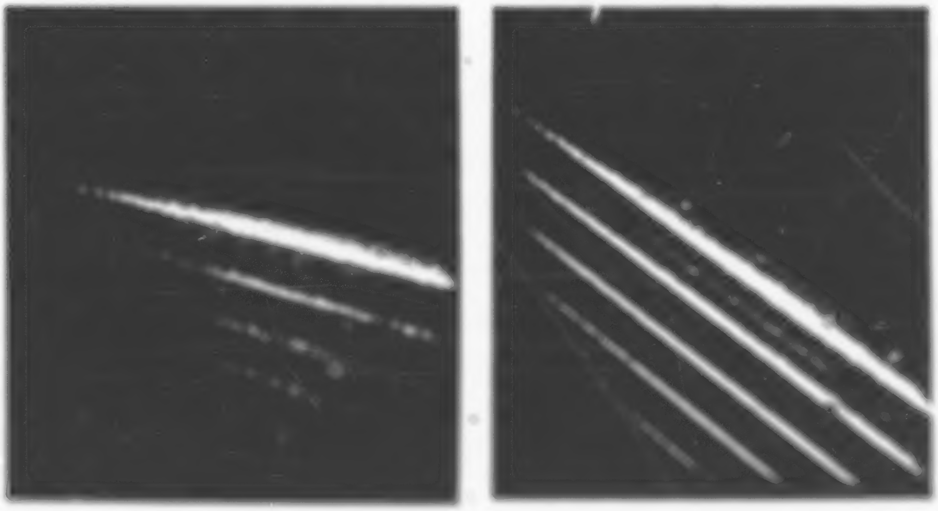
Fig. 13: View on the combustion chamber wall



With calcium injection
Boiler height: 49 m

Without calcium injection
Boiler height: 49 m

Fig. 16: Slagging in furnace



With calcium injection
Boiler height: 74 m

Without calcium injection
Boiler height: 74 m

Fig. 17: Fouling on convection heating surfaces

Figure 13 shows the x-ray diffraction analysis of fly-ash at full load without limestone, fly ash at full load with limestone in the proportion Ca/S = 0.33, fly ash at 50% load with additive again in the proportion Ca/S = 0.33 and superheater fouling deposits with limestone injection. The components are identified in the order shown.

In the uncontaminated fly ash there is a certain degree of sulfur capture by calcium naturally occurring in the coal. A very small amount of free CaO is also present.

Injection of limestone around the flame increases the degree of sulfur capture. $CaSO_4$ is no longer the last component but ore; instead it is now the last component but 2 and no $CaSO_3$ can be found. This is important for futher processing and possible dumping.

Mainly bcause of the lower furnace temperatures involved, sulfur capture is sigificantly better at low load. $CaSO_4$ moves up one place in comparison to its listing at full load.

The supeneater fouling deposits on the boiler side where limestone was injected cntain the highest quantities of $CaSO_4$ and the level of free CaO is very low.

Figure 1[illegible] shows the theoretically calculated ash composition for direct desulfuization on all burners. The Göttelborn coal from the Saar region used at Weiher power station is reckoned to have an ash content of 8%.

For a molr ratio Ca/S = 2, the original fly ash makes up 61% of the total and cacium products are composed as follows: CaO = 21%, $CaSO_4$ = 17%, $CaCl_2$ = 0.5% and $CaF_2$ = 0.1%. At a molar ratio of Ca/S = 4, the original fly ash makes up only 45% of the total fly ash, the rest being calcium poducts.

These resiues are naturally not officially certifiable for use, like a normal fly ash. However, Steinmüller is investigating the possibility of utilizing these residues in the building material industry.

CURRENT ACTIVITIES

(a) Weiher III Power Station

After the preliminary tests on two burners proved positive, we are now equipping all 24 for direct desulfurization. The tests should begin at the end of this year.

(b) 30 MW Burner at EER in the USA

A 30 MW burner is being tested this year in the United States. Besides Göttelborn coal, two American bituminous coals are being used.

| Fly ash at full load | Fly ash at full load | Fly ash at half load | Deposits on superheater with lime injection |
|---|---|---|---|
| $Ca/S = 0$ | $Ca/S = 0,33$ | $Ca/S = 0,33$ | |
| $SiO_2$ | $SiO_2$ | $SiO_2$ | $CaSO_4$ |
| $3Al_2O_3 \cdot 2SiO_2$ | $CaO$ | $CaO$ | $Fe_2O_3$ |
| $Fe_2O_3$ | $3Al_2O_3 \cdot 2SiO_2$ | $CaSO_4$ | $SiO_2$ |
| $Fe_3O_4$ | $CaSO_4$ | $3Al_2O_3 \cdot 2SiO_2$ | $3Al_2O_3 \cdot 2SiO_2$ |
| $CaSO_4$ | $Fe_2O_3$ | $Fe_2O_3$ | $K_2Mg_2(SO_4)_3$ |
| $CaO$ | $Fe_3O_4$ | $Fe_3O_4$ | $CaO$ |
| Amorphous components | Amorphous components | Amorphous components | $MgO$<br>$Fe_3O_4$ |

X-Ray Diffraction Analysis

Fig. 18

## Göttelborn Coal

| | | Ca/S = 2 | Ca/S = 4 |
|---|---|---|---|
| Fly ash | % | 61,1 | 45,4 |
| CaO | % | 21,0 | 33,6 |
| $CaSO_4$ | % | 17,3 | 20,5 |
| $CaCl_2$ | % | 0,5 | 0,4 |
| $CaF_2$ | % | 0,1 | 0,1 |

Ash Composition with Direct Desulfurization

Fig. 19

(c) DeNO$_x$/DeSO$_x$ Firing System in Canada

We have already completed a study on a DeNO$_x$/DeSO$_x$ firing system for CFB Gagetown in Canada and have received a contract for the hardware. The commissioning should take place in the middle of next year.

(d) Combustion of Petroleum Coke at IFRF/Ijmuiden

Direct desulfurization in petroleum coke combustion has been experimentally investigated on a 3 MW burner at IFRF/Ijmuiden, as part of a larger R&D program.

(e) Direct Desulfurization on Travelling-Grate Stoker Firing

We have recently booked an order for applying in-furnace desulfurization to a steam generator of 100 MW thermal capacity equipped with a travelling-grate stoker firing. The commissioning should take place in the middle of next year.

Thus, by the middle of next year, we shall have gained a great deal of additional experience in the area of direct desulfurization.

## SESSION 5: DUAL ALKALI

Chairman: Norman Kaplan
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC

# UTILITY DOUBLE ALKALI OPERATING EXPERIENCE

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## ABSTRACT

On April 6, 1983, Northern Indiana Public Service Company started up its Schahfer Unit 17, the first high sulfur coal boiler required to be in compliance with the 90% $SO_2$ removal provision of the 1979 revisions to the New Source Performance Standards. This is the fourth utility double alkali FGD system to come on line in the last four years. All have consistently met their $SO_2$ performance criteria. This paper summarizes cost and availability data for three of these systems. While capital costs vary with site specific design criteria, operating costs exclusive of capital charges are typically 4 mills/kWh. Availabilities for the double alkali systems as a group are consistently higher than for direct limestone. Unique features of the NIPSCO design and operation are discussed as well as some important recent improvements implemented at the Southern Indiana Gas and Electric and Central Illinois Public Service Company installations.

## INTRODUCTION

The double alkali process is a second generation throw-away FGD technology that was first offered commercially to the utility industry in 1975. A fundamental characteristic of the process is its capability to achieve very high efficiencies reliably even on very high sulfur dioxide concentrations. This makes the process particularly appropriate for high sulfur Eastern coals, especially in light of the 1979 revisions to the New Source Performance Standards which mandate 90% removal on a continuous basis.

Since 1975, six double alkali systems have been sold, all in the high sulfur coal Midwest. Three of these systems were started up in 1979, and the fourth, Northern Indiana Public Service Company's R. M. Schahfer Unit 17, was started up this spring. The two remaining units are scheduled to start-up in 1986.

The purpose of this paper is to consolidate and bring up to date the noteworthy developments of the past two years at these installations. Special features of the NIPSCO system design are reviewed along with the early performance and start-up results. In addition, two of the three systems that have been in operation since 1979 (Southern Indiana Gas & Electric Company's [SIGECO] A. B. Brown Unit 1 and Central Illinois Public Service Company's [CIPS] Newton Unit 1) have undergone important modifications in the last few years. These modifications are discussed and the key operating results (emissions performance, reliability, and cost) are presented for the three systems as a group.

## SCHAHFER UNIT 17 DESIGN

### DESIGN CRITERIA

NIPSCO's Rollin M. Schahfer Generating Station is located on the Kankakee River near Wheatfield in northwestern Indiana. The two newest units at the station, 17 and 18, have a gross generating capacity of 393 megawatts each. These units, for which construction began in 1980, are the first ones built under the revised New Source Performance Standards provision requiring 90% sulfur dioxide removal on a continuous 30-day rolling average basis. Each unit has a design heat input of 3,967 x $10^6$ Btu's per hour and a flue gas flow at the FGD system inlet of 1,591,500 acfm at 327°F. The performance coal data are given in Table 1.

TABLE 1. PERFORMANCE COAL DATA

| | (Percent by weight) | | | | |
|---|---|---|---|---|---|
| | Typical | | Range | | |
| | As Rec'd | Dry Basis | As Received | | |
| Moisture | 11.25 | - | 9.70 | - | 13.10 |
| Carbon | 61.64 | 69.45 | 57.36 | - | 63.09 |
| Hydrogen | 4.53 | 5.10 | 4.33 | - | 4.90 |
| Nitrogen | 1.12 | 1.26 | 1.06 | - | 1.31 |
| Chlorine | 0.02 | 0.02 | 0.01 | - | 0.02 |
| Sulfur | 3.20 | 3.61 | 2.60 | - | 3.57 |
| Oxygen (diff.) | 7.90 | 8.90 | 6.99 | - | 8.43 |
| Ash | 10.34 | 11.66 | 7.80 | - | 13.90 |
| Total | 100.00 | 100.00 | - | | - |
| Heating Value (Btu/lb) | 11,085 | 12,490 | 10,500 | | 11,600 |

Key requirements of the specificaton include:

1. Four absorbers per unit (three operating and one spare).
2. All alloy construction in the absorbers and downstream ductwork with no bypass.
3. Thirty degrees Fahrenheit of inline reheat.
4. Two complete regeneration trains per unit, each capable of supporting the system at 67 percent of full load using the maximum sulfur fuel.
5. Waste product stabilization designed to allow blending of all of the fly ash from Units 17 and 18 plus Units 14 and 15 with the FGD waste product.

## PROCESS DESIGN

The NIPSCO system utilizes the conventional concentrated double alkali process furnished by FMC Corporation. Figure 1 is a schematic representation of the process. Sulfur dioxide is absorbed according to the following reaction:

$$Na_2SO_3 + SO_2 + H_2O \longrightarrow 2NaHSO_3 \qquad (1)$$

Sodium bisulfite formed in the absorber is removed from the absorber loop as a bleed stream to a separate lime mixing tank where it is reacted with hydrated lime to precipitate primarily calcium sulfite according to the following reaction:

$$2NaHSO_3 + Ca(OH)_2 \longrightarrow Na_2SO_3 + CaSO_3 \cdot \frac{1}{2}H_2O + 1\frac{1}{2}H_2O \qquad (2)$$

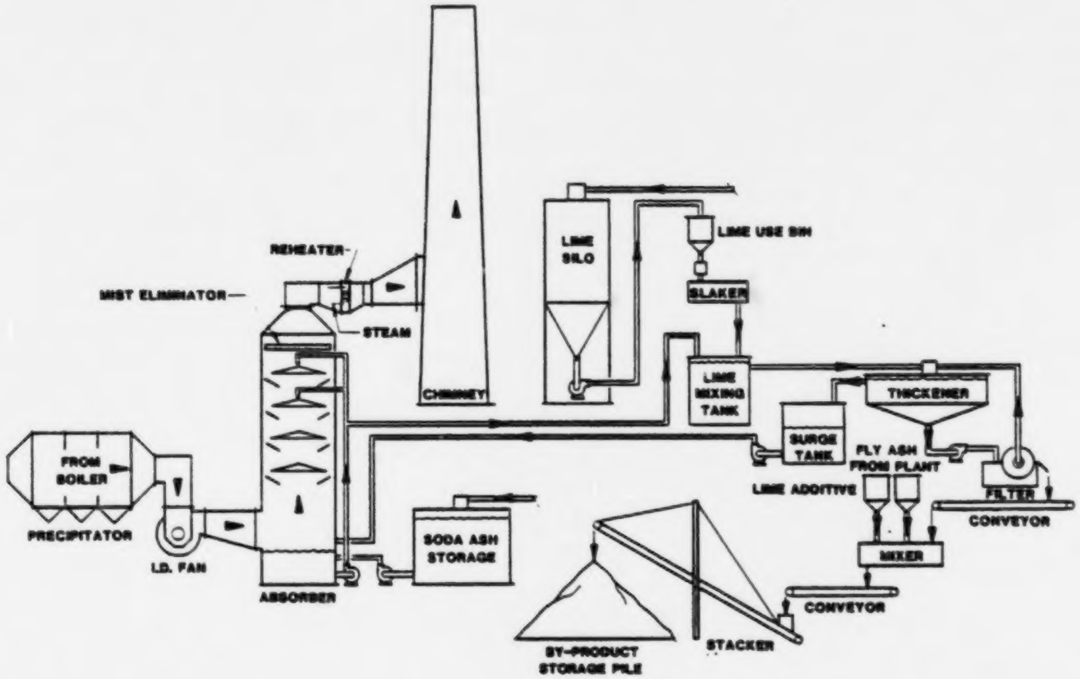

Figure 1. NIPSCO FGD PROCESS SCHEMATIC

The sodium sulfite that is regenerated by the above reaction is returned to the scrubbing process for reuse. The small amount of sodium that is not recoverable is replaced through the addition of soda ash to the scrubbing system. The pH of the sodium scrubbing solution is maintained at a level which buffers the scrubbing system and eliminates calcium scaling.

## FACILITIES DESCRIPTION

The NIPSCO facility is depicted schematically in Figure 1 and in plan view in Figure 2. The gas side control loops for Unit 17 and the future Unit 18 are independent of each other and under the control of the boiler control room operating personnel. The regeneration portion of the process, however, is integrated for Units 17 and 18 and under the control of FGD area operating personnel in an area several hundred feet away from the absorber area. The regeneration facility will ultimately contain four independent regeneration trains, each capable of accommodating two-thirds of the capacity of each boiler when operating on its maximum sulfur fuel. Under normal sulfur and load operating conditions, the regeneration area has effectively 100% spare capacity.

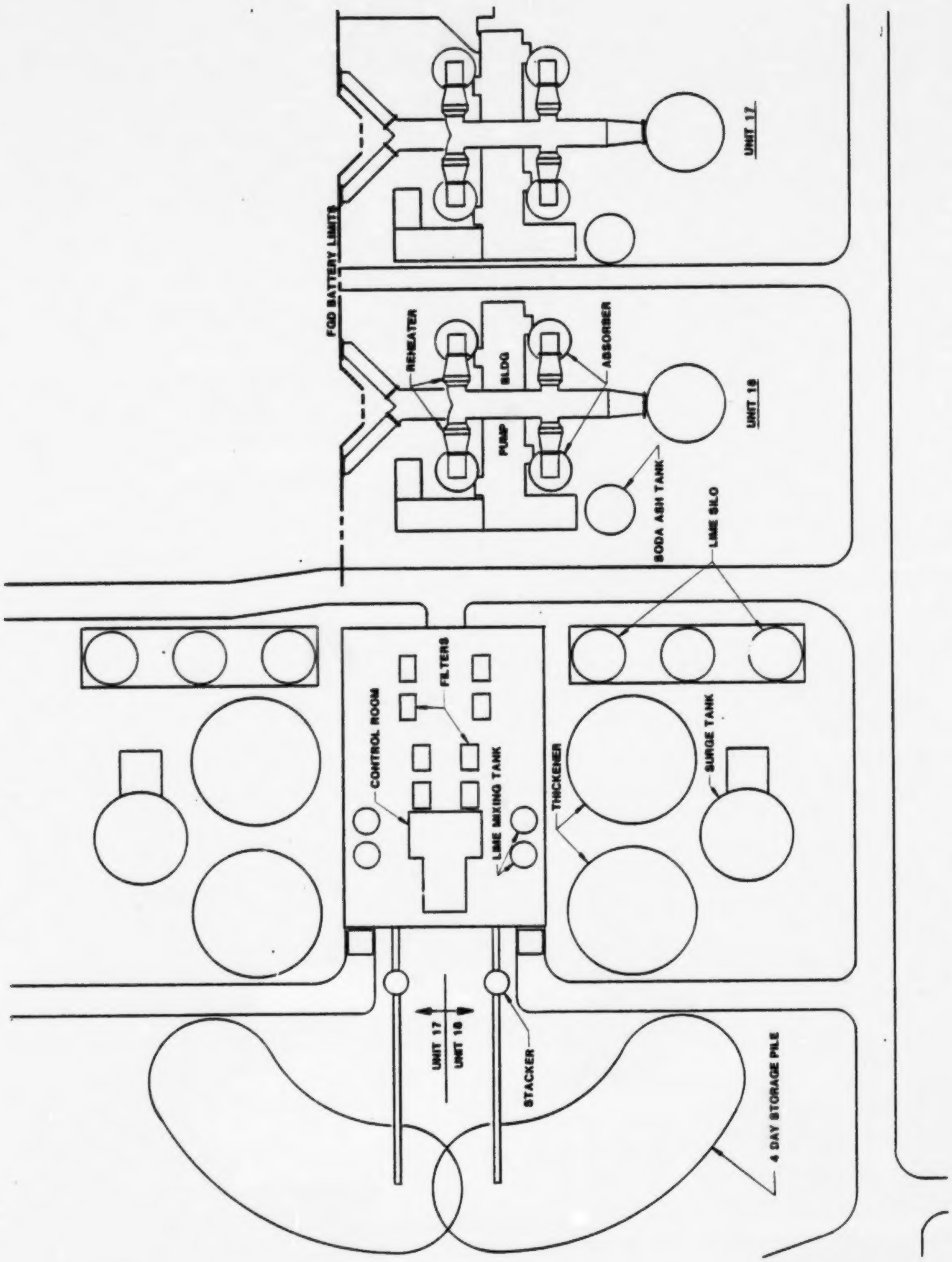

Figure 2. NIPSCO FGD AREA PLAN

The flue gas leaves the boiler and enters the rigid frame electrostatic precipitator. Immediately downstream of the precipitator are the induced draft fans which draw the flue gas through the boiler and pressurize the FGD system. Flue gas enters the bottom of the 32-foot-diameter absorbers. These absorbers are constructed of 317LM stainless steel and consist of four disc and donut absorption stages. A concentrated solution of sodium sulfite is pumped from the sump in the base of each absorber to the top of the absorber at a liquid-to-gas ratio of approximately 10 gal/Macf. The scrubbing solution cascades through the absorption stages while the gas flows countercurrent through the stages, to the top of the absorber. Two 100% capacity alloy (317LM) pumps per absorber continuously recirculate the solution and bleed off the spent solution to the regeneration area.

Installed in the upper level of each absorber is a mist eliminator constructed of 904L stainless steel. From the mist eliminator, gas exits each absorber and passes through an in-line steam reheater, constructed of Inconel 625, which provides 30°F of reheat. From there the gas enters a common outlet duct to the 500-foot-tall acid brick-lined chimney.

Proportionate to the amount of $SO_2$ collected, the absorber bleed stream is pumped to one of the two lime mixing tanks located in the regeneration building. There, slaked lime from the six slakers (2 spare) is added to the continuously agitated tanks to regenerate the sodium sulfite and form by-product solids. Each lime tank overflows by gravity to a 90-foot-diameter thickener which concentrates the calcium sulfite solids. Regenerated scrubbing solution overflows by gravity to a single regeneration surge tank, from which it is pumped on demand to the absorbers.

The thickener underflow is pumped by air-operated diaphragm pumps to four 33% capacity rotary drum vacuum filters. The filter cake is washed on the vacuum filters with heated water to recover additional sodium. Sodium remaining in the filter cake is replaced by adding soda ash ($Na_2CO_3$) in the regeneration return line from the surge tank.

The filter cake is transported by conveyor to one of the four mixers. The cake is mixed with flyash and pulverized lime to increase strength and reduce permeability.

The FGD by-product is conveyed to one of two radial stackers, serving both Units 17 and 18, and is discharged to a temporary disposal area. Then the material is loaded onto 50-ton off-road trucks for hauling to the on-site product disposal area located about one mile east of Unit 17. The material is placed and compacted to a maximum height of 67 feet. The approximately 200 acre disposal area will be covered with soil and seeded as each section is completed.

## NIPSCO START-UP

NIPSCO's Schahfer Unit 17 started up on April 6, 1983, and the FGD system was first operated on April 10. The unit was declared commercial on April 28. Unfortunately, in addition to the FGD area problems which will be discussed below, there have been numerous outages initiated by events upstream of the FGD system. These outages have prevented the collection of much meaningful data on cost or reliability in the FGD area. However, official plant records indicate that the FGD system has theoretically constrained the boiler load only 5.3% of the time so far.

Aside from the usual list of start-up trials and tribulations, there are a few aspects of the early operation that are noteworthy or unique.

### ABSORBER PERFORMANCE

The disc contactor scrubbers are guaranteed to achieve 90% sulfur dioxide removal with three stages in operation at a design liquid-to-gas ratio of 10 gal/Macf. However, early spot checks based on the $SO_2$ monitor indicated that efficiency was frequently in the 80's. Closer examination showed that the design efficiency was not being achieved under certain combinations of flow conditions, apparently due to maldistribution of the flue gas. This had the effect of short-circuiting the bottom stage of the absorber. In June and July, three different inlet baffling arrangements were tested. The best of these arrangements was implemented on all absorbers in August and unofficial performance tests on the individual absorbers showed that 90% efficiency was being achieved routinely with three stages. These results are given in Figure 3, which shows collection efficiency as a function of number of stages in operation and percent of design flow rate. These results correlate excellently with an existing design model which expresses number of transfer units as a function of liquid-to-gas ratio, superficial gas velocity, and certain dimensions of the absorber. However, the cause of the gas maldistribution problem is still something of a mystery in that other existing absorbers of a very similar design have not experienced this problem and there is no significant maldistribution of the velocity profile entering the absorber.

### VIBRATION

During start-up, severe vibration was noted in the outlet ductwork and reheater casing of the FGD system. Initially, effects of the vibration were limited to the loss of the outlet instrumentation (pressure and temperature) due to the instrumentation and instrumentation taps being cracked and/or broken. Next, a crack was noticed in the absorber shell. The crack had propagated from the toe of an internal weld. Further investigation identified cracks throughout the outlet ductwork from the absorber outlet elbow to the guillotine damper. All cracks started in an area where there was internal or stitch welding performed. A dye penetrant test was conducted on the outlet ductwork to ensure all cracks were found and repaired.

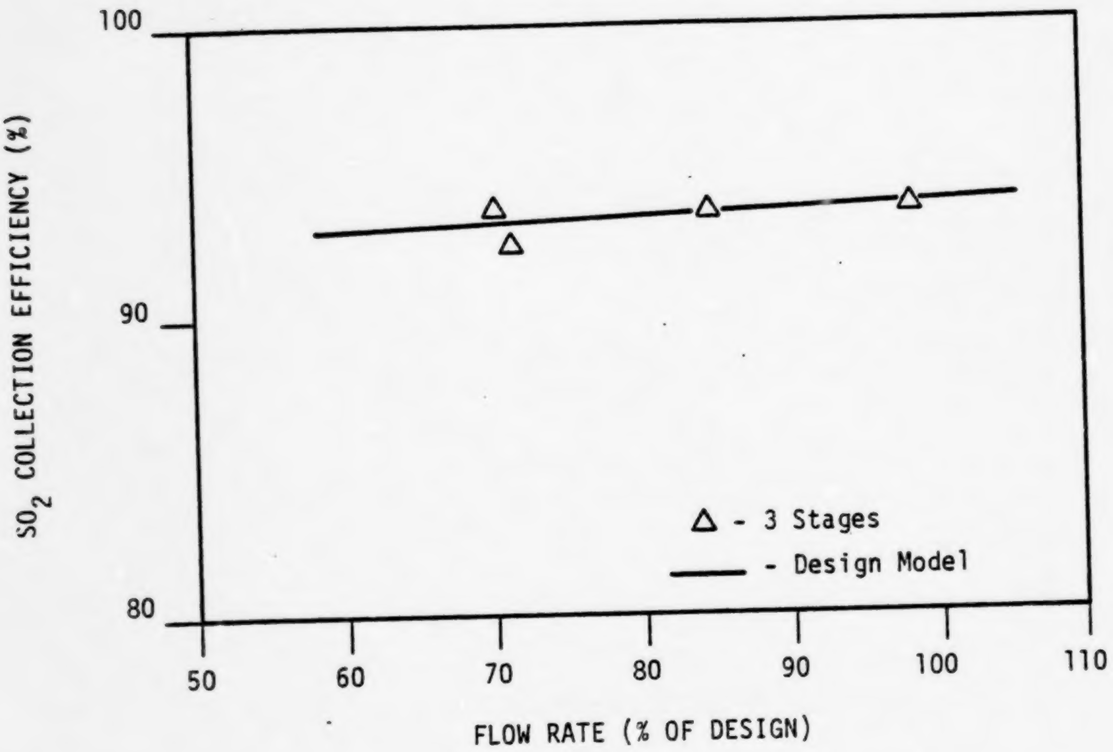

Figure 3. UNOFFICIAL COLLECTION EFFICIENCY VS. GAS FLOW RATE

Extensive testing was carried out in conjunction with Stone and Webster and NIPSCO to determine the cause of the vibration. Testing results centered around the reheater and the turning vanes in the outlet elbow. Vibration was occurring at the two resonant frequencies of the ductwork. Further testing indicated that the excitation was flow related. The larger of the two turning vanes was removed as shown in Figure 4, and blanking plates were installed at the top of the reheater housing. These changes greatly reduced the vibration, but it reappeared with somewhat lower intensity.

As in the first instance, the source of the vibration could not be identified. It appeared to be amplified by the steam tube reheaters and certain dimensions of the ductwork that approximated multiples of the wavelengths corresponding to the natural frequency of the structure. On this occasion it was found during in situ air tests that there was boundary layer separation at the diverging sidewall section of the ductwork between the outlet elbow and the reheater (see Figure 4). Four foot wide test panels installed at each side of the inlet to the reheater perpendicular to the gas stream eliminated the vibration completely but were deemed impractical because of their obvious adverse effects on the reheater performance. An alternative solution found by trial and error turned out to be the installation of a perforated plate along the bottom of the outlet of the elbow between the smaller turning vane (see Figure 4) and the bottom of the duct. However, there is still no satisfactory explanation for why this modification worked.

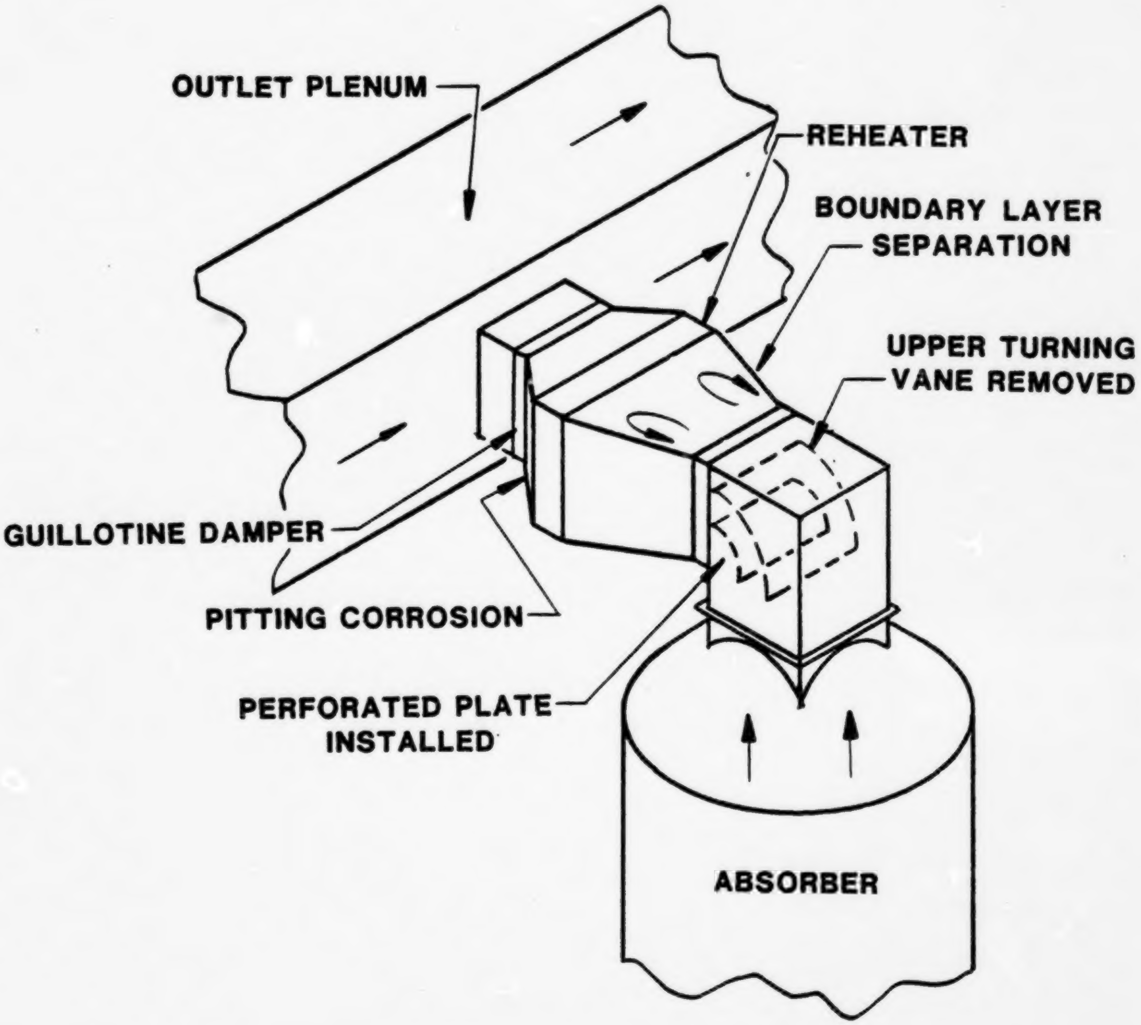
OUTLET PLENUM
REHEATER
BOUNDARY LAYER SEPARATION
UPPER TURNING VANE REMOVED
GUILLOTINE DAMPER
PITTING CORROSION
PERFORATED PLATE INSTALLED
ABSORBER

Figure 4. ABSORBER OUTLET DUCTWORK ISOMETRIC VIEW

## MATERIALS OF CONSTRUCTION

During the engineering of the FGD system, NIPSCO evaluated two materials of construction alternatives in some detail. The first alternative was flake-glass-filled polyester resin linings for the absorbers with full bypass and quench protection for the lining. The second alternative was all alloy construction with no bypass. For the relatively high pH of the double alkali process (6 to 7) and the relatively low chloride concentrations anticipated (less than 6,000 ppm), 317LM stainless steel was selected as the principal alloy for the absorbers. Based on this alloy selection, the alloy absorber option evaluated better than lining when the implications of the quench system, bypass, and associated dampers and draft control requirements were taken into account.

An inspection of the absorber and ductwork internals in early August revealed two areas of concern. First, the cracks in the outlet duct mentioned in the preceding section were examined more closely. Test specimens were removed and analyzed, but corrosion of the fracture surface made it impossible to determine for certain if the cracks were initiated by stress corrosion or fatigue. It is clear that the cracks propagated in fatigue and the circumstantial evidence of the vibration and the nature of the cracks strongly suggest that they were fatigue initiated. All of these cracks have been ground out and repaired and only time will tell if the elimination of the vibration has also eliminated the cracking.

A second area of concern is the small section of ductwork between the reheater and the outlet isolation damper for each absorber module (about 7% of the total outlet duct area; see Figure 4). The converging sidewalls in this relatively short segment of ductwork show varied degrees of pitting. These converging walls, which experience impingement of the flue gas stream and intermittent saturated and unsaturated conditions due to the intermittent operation during start-up, are obviously high potential sites for corrosion. Test coupons have been installed in one of these duct segments and will be monitored closely to provide data on possible alternate materials in this area.

The outlet plenum and the absorbers themselves are overall in excellent condition with only one or two localized areas of pitting identified at this time.

## CIPS UPDATE

Central Illinois Public Service Company's, Newton Unit 1 FGD system distinguished itself in 1982 with a 97.8% availability record, the best record of any high sulfur coal FGD system reporting to EPA for the full year. Recent developments at CIPS that are of general interest are discussed below.

## PROCESS MODIFICATIONS

The Newton double alkali FGD system began operation in a double loop mode with a unique precooler loop which removed chlorides from the flue gas before scrubbing for $SO_2$. The objective was to reduce reagent consumption and protect the system from corrosion. Extensive problems associated with this loop greatly reduced overall system availability during the first eight months following start-up. These problems were substantially eliminated by CIPS through modifications which eliminated the chloride removal function of the precooler loop.

CIPS subsequently applied for a patent to cover these system modifications, which included:

1. Changes in system pH;
2. Reaction residence times; and
3. Alteration of agitation and tip speed in the reaction tanks.

In May of this year, CIPS received Official Notice of Allowance for the patent application and is currently working through its patent attorneys to finalize the paperwork on the patent, which is expected to issue October 25, 1983.

## SYSTEM PERFORMANCE

The Newton system was designed to maintain compliance with Subpart D of the New Source Performance Standards. As such, it is required to meet a 1.2 lb/MMBtu $SO_2$ emission limit, but has no requirement for removal efficiency. Accordingly, no inlet $SO_2$ monitors are used on the system, and there have been no Method 6 inlet/outlet efficiency tests conducted.

The coal burned in Unit 1 has an average sulfur content of approximately 2.8% (or about 4.5 lb/MMBtu $SO_2$).

In conducting tests associated with optimization of scrubber performance over the last several years, it has been demonstrated that the absorbers can achieve outlet loadings of less than 0.6 lb/MMBtu. In addition, between September 1980 and June 1982, five audits conducted by a US EPA contractor demonstrated that outlet levels in the 0.3-0.6 lb/MMBtu range had been achieved.

## LIMESTONE CONVERSION

CIPS is presently studying the feasibility of converting the lime-based double alkali system at Newton to limestone-based. Obviously, such a conversion would have significant cost benefits by substantially reducing the reagent cost component of the operation. Concerns include the following impacts such a conversion might have on the process itself:

1. Will efficiency and system control be similar to present operation?
2. How will a conversion affect filter cake solids concentrations and quality?
3. Impact on soda ash consumption and regenerated liquor quality.

All testing to date indicates such a conversion would be quite cost beneficial and technically sound.

## SIGECO UPDATE

In spite of the excellent performance record in terms of compliance operation, availability, and cost compiled at A. B. Brown Station in its four years of operation, SIGECO has continued to strive to reduce its costs and further improve its reliability. In the last few years, this effort has centered on improvements in equipmment design for those components which caused the greatest percentage of the forced outages. Additional efforts have centered on improvements in filter cake quality as has been reported at the last two symposia.* Solids quality affects the quantity of material, placement cost in the landfill, and the maintenance and reliability in the material handling segment of the system. Additionally it relates directly to reagent consumption.

In 1982, SIGECO initiated a program to improve the regeneration section of the system. This program centered around crystal growth studies conducted by Codan Associates and a series of equipment design changes engineered by FMC and implemented by SIGECO plant engineering.

### EQUIPMENT MODIFICATIONS

In late 1982 the design changes planned for A. B. Brown were detailed by FMC. Beginning in the second quarter of 1983 they were implemented by SIGECO plant engineering. The status of the major changes is summarized below:

1. The existing lime reactor was modified in April in accordance with Codan's recommendations. The average moisture content of the cake for the month prior to the shutdown was 48.1%. For the month immediately after the system was restarted in May, the moisture content averaged 41.7%. This 6.4% increase in solids content resulted in relatively dramatic improvement in the cake consistency.

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* Durkin, T. H., Wilhelm, J. H., Boward, W. L., "Recent Operating Results with the Double Alkali Process," EPA Symposium on Flue Gas Desulfurization, Hollywood, FL, May 1982.

Van Meter, J. A., Durkin, T. H., Legatski, L. K., "Operating Experience with the FMC Double Alkali Process," EPA Symposium on Flue Gas Desulfurization, Houston, TX, October 1980.

2. A horizontal bed filter was installed in summer 1983 and started up in early September. The horizontal filter replaces one of the three original rotary vacuum filters, though it has sufficient capacity to carry the system at full load by itself. The other two rotary filters are being retained as back-up. The filter was started up early in September, and it further improved the solids content of the cake while increasing filtration rates to 75 - 100 lb/hr-ft$^2$.

3. The original thickener rake has been replaced with a power lift rake, and other modifications have been made to allow the thickener to function as a reactor as well as a thickener. Late this year the existing lime reactor will be converted into a lime slurry storage tank, and the reaction step will be moved to the thickener. The availability of a lime slurry storage tank and the power lift thickener should eliminate the sources of two of the most important causes of forced outages in the past.

SIGECO is optimistic that these changes will meet its stated objectives* of improving the availability to 99% from the recent availability of 91.1% and further reducing current operating costs of 4 mills/kWh by 0.5 - 0.7 mills/kWh.

## CRYSTAL GROWTH STUDIES

The characterization of waste solids from FGD systems, both direct lime and limestone and double alkali, is a deceptively complex subject. Relatively large differences in solids quality between different commercial FGD systems have been noted but not explained in any systematic way. The problem is complicated by the lack of clear-cut criteria for solids quality. For example, percent solids is not by itself a meaningful criterion. A forced oxidation system producing a calcium sulfate (gypsum) product at 80% solids generates the same mass of material for disposal as an unoxidized calcium sulfite producing system that generates 60% solids. Moreover, a higher percent solids material may or may not be superior in terms of handleability, bearing strength or permeability. These latter characteristics depend primarily on the size and shape of the crystals produced rather than just solids content. However, when comparing cake quality in chemically identical situations, percent solids is usually a fair measure of solids quality.*

It has been found that the crystal size and shape in double alkali FGD are primarily influenced by the following variables:

1. Reactor residence time
2. Shear rate of the agitator(s)
3. pH
4. Concentration of solids
5. Magnesium concentration
6. Entry point of the reactants

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* Durkin, et al., op. cit.

7. Lime slaker design and operation
8. Chloride concentration
9. Sulfate concentration
10. Sulfite and bisulfite concentrations
11. The presence of other crystal modifiers
12. Chemical composition of the lime used

It is outside the scope of this paper to review the influence of each of these variables. However, it is important to note that the current study by Codan showed that through minor changes in agitator speeds, operating pH and points of addition of reactants to the reactors, the crystal size and dewatering characteristics could be improved substantially. For the A. B. Brown system, as with CIPS' Newton station which was modified a few years ago, it has been shown that the filter cake solids content can be increased from 10 to 20 weight percent even though the chemical conditions at the two systems are different and the modifications required to achieve the improvement in solids quality are not identical. This improvement in solids content corresponds to reducing the weight of water per weight of dry solids by as much as half, and it results in much improved cake washing efficiencies and handling characteristics of the dewatered cake. The dewatering rates are also improved substantially, resulting in smaller equipment sizes required for thickening and filtration.

Figure 5, which is based on data obtained by Codan for CIPS a few years ago, is an example of the type of improvement that can be made by adjusting agitator speed. In this particular instance, the higher agitation speeds cause a deterioration in filter cake solids concentration. By lowering the agitator speed (shear rate) at the time the solids are precipitated, the final crystal size is improved, thus improving cake solids concentration. Similar effects were obtained with the use of high calcium lime and magnesian lime, but the shape of the curves and the required operating pH may be different. Reactor residence time also changes the shape of the curve shown in Figure 5.

It is interesting to note that some of these reaction variables apply to lime and limestone scrubbing systems also. This has been shown to apply particularly to agitation, magnesium concentration, residence time, pH and chemical composition of the lime or limestone used. The presence of co-precipitates such as sulfate and magnesium has a marked effect on the influence of agitation and detention time.

## OPERATING RESULTS

Ultimately, there are really only three important criteria for a flue gas desulfurization system. These are:

- Can it meet the legislated emissions criteria?
- Is it reliable and available? That is, can it meet the emissions criteria consistently with acceptable levels of maintenance and operator attention?

- Is it cost competitive?

Double alkali clearly meets all of these criteria based on the three systems discussed here when considered individually or as a group.

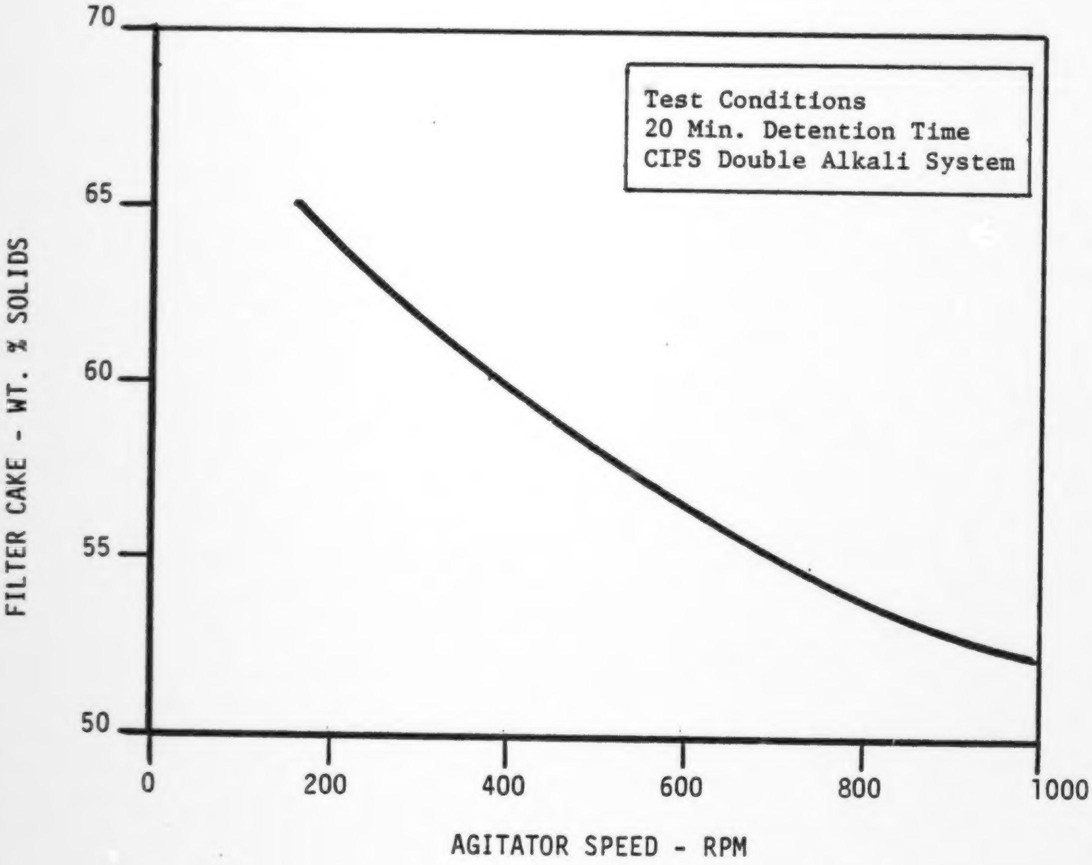

Figure 5. EFFECT OF AGITATOR SPEED ON FILTER CAKE SOLIDS CONCENTRATION

## EMISSIONS PERFORMANCE

The sulfur dioxide removal performance of all three systems is summarized in Table 2.

## TABLE 2. UTILITY DOUBLE ALKALI SULFUR DIOXIDE REMOVAL SUMMARY

| | SIGECO | CIPS | NIPSCO |
|---|---|---|---|
| Station Name | Brown 1 | Newton 1 | Schahfer 17 |
| Unit Sizes | 265 | 575 | 393 |
| Coal Sulfur Content, % | 3.4-4.5 | 2.8 | 3-3.7 |
| Inlet Sulfur Dioxide Concentration | | | |
| (ppm dry) | 3,100-4,000 | -- | 1,700-2,700 |
| (lb/MMBtus) | -- | 4.5 | — |
| Outlet Sulfur Dioxide Concentration | | | |
| (ppm dry) | 240-300 | -- | 132-215 |
| (lb/MMBtu) | -- | 0.3-1.1* | 0.49 |
| Efficiency (%) | 85-93 | -- | 92 |
| Regulation | 1.2 lb/MMBtu | 1.2 lb/MMBtu | 90% and 0.62 lb/MMBtu |

*Newton 1 has achieved outlets of 0.3 to 0.6 in individual tests, but normally operates at 1.0 to 1.1.

Even though the absorber designs and process conditions are slightly different in each case, all three systems clearly meet their regulatory requirements with room to spare.

## AVAILABILITY

Availability results as reported in the current PEDCO data base for 1982 for A. B. Brown 1 and Newton 1 are summarized in Figure 6. However, the record should reflect that SIGECO subsequently recognized that they counted the system as available during two major outages totaling 30 days during which duct and absorber lining repairs were made. They have recently asked PEDCO to correct the official record to reflect this, but this change has not yet been made in the PEDCO data base. The only significant forced outage at Brown during 1982 was attributable to freezing the plant water system during January.

For all of 1982, SIGECO's records indicate that Brown 1 was in compliance 89 - 91% of the time based on hourly monitoring and material balance methods respectively. More recently, in anticipation of future increased load demand for Unit 1, they have begun to keep track of their "full load capability." Full load capability represents SIGECO's assessment of its ability to stay in compliance under boiler design maximum operating conditions. SIGECO has retroactively estimated their full load capability for 1982 as 80%, and they are committed to a goal of raising it to 85%. Given that Brown has no spare absorber and very little spare equipment in other areas, this is an impressive objective.

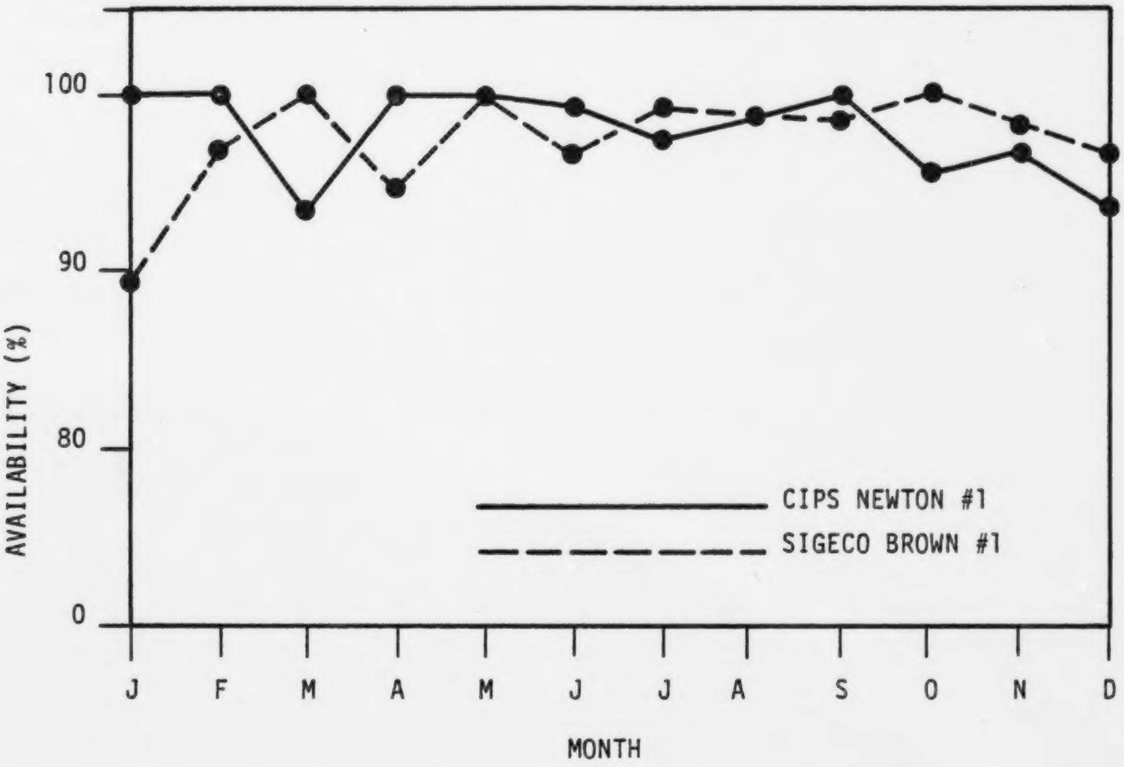

Figure 6. 1982 PEDCO DOUBLE ALKALI SYSTEM AVAILABILITIES*

*SIGECO data include 30 days of scheduled outages counted as available time

Availability results for all high-sulfur-coal FGD systems reporting availabilities and operating costs to EPA from mid-1981 to mid-1982 are summarized in Figure 7. The fuel sulfur contents are the reported design basis. However, CIPS and SIGECO's actual sulfur contents are 2.8 and 3.8% respectively. Costs include capital and various adjustments made by PEDCO to put systems on a comparable basis. These results reflect the superior availability record of the double alkali process in high sulfur coal applications. It is too early to tell whether the NIPSCO system will continue that record. However, the system is guaranteed to be 97% available without the use of the spare absorber during a 90-day test period scheduled later this year, and there is presently no reason to believe that it will fail to pass that test.

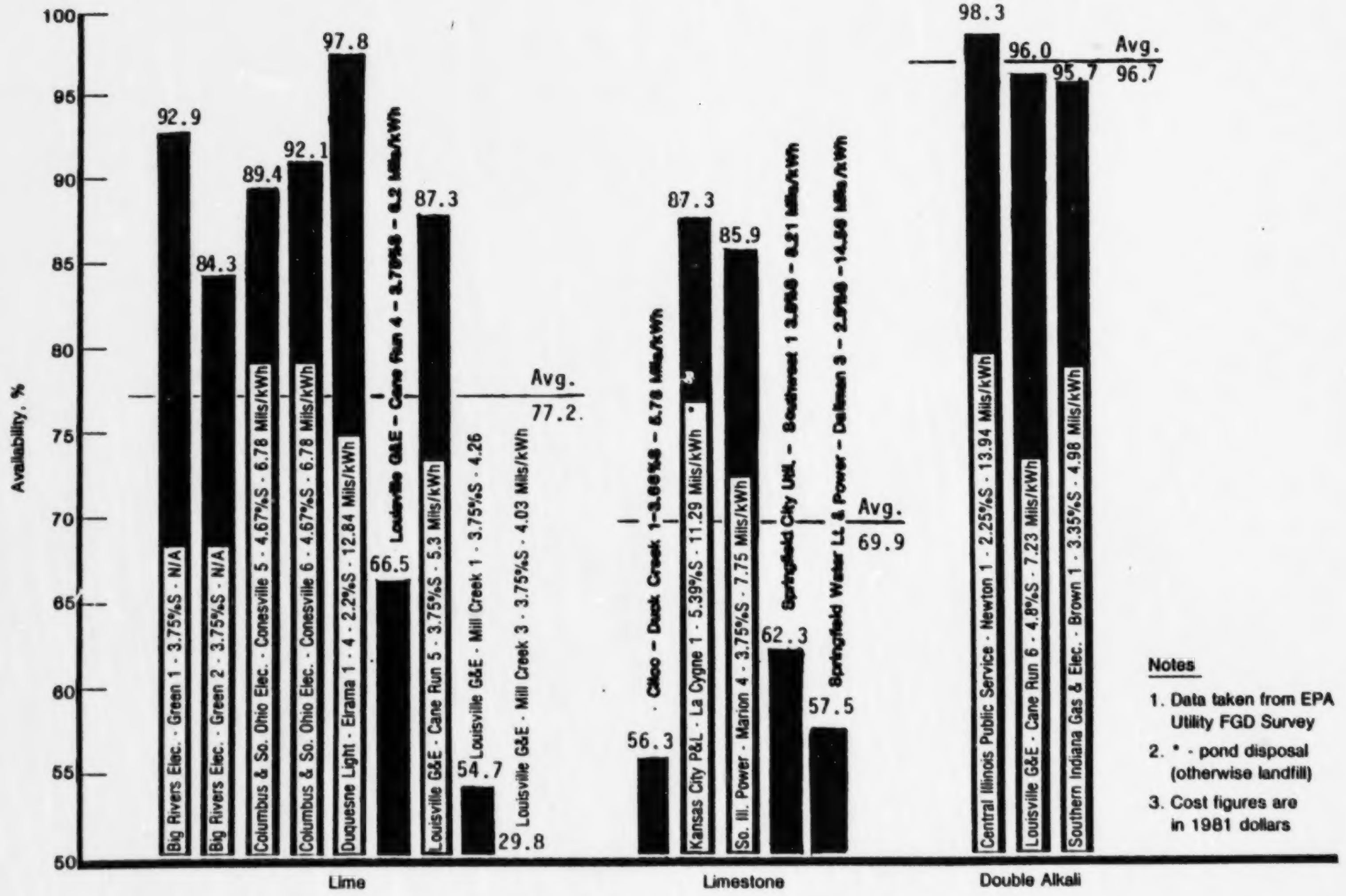

Figure 7. FGD SYSTEM AVAILABILITY JULY 1981 TO JUNE 1982 (>2%S)

## OPERATING COSTS

Operating costs are difficult to compare because they are not always recorded on a consistent basis and they reflect significantly different design conditions, unit costs, and capital charges.

Capital costs vary more with respect to site specific design requirements than they do according to process type. For similar design criteria, all wet FGD systems have similar costs for reagent preparation, ductwork, dampers, reheaters, and absorbers, which as a group typically comprise 70-80% of FGD system cost. For consistent design criteria, none of these components of the cost is more expensive for double alkali than for any other wet FGD system.

Non-capital operating costs for 1982 for Brown 1 and Newton 1 are reflected in Table 3. These numbers include disposal. The total costs for the two systems are very close, even though the respective circumstances are slightly different. SIGECO has higher reagent costs, reflecting its higher sulfur fuel, but lower operating labor and maintenance costs, primarily because it does not include a stabilization system and the general arrangement allows them to cover the area with less people. Power costs for SIGECO are slightly less because of the double loop scrubber design at CIPS. In all cases, these costs are lower than the values for the comparable line items in the most recent EPRI sponsored process evaluation which overall showed lime regenerated double alkali to be very competitive with conventional limestone scrubbing.

TABLE 3. 1982 DOUBLE ALKALI OPERATING COST SUMMARY

| | A. B. BROWN 1 | NEWTON 1 |
|---|---|---|
| Cost Item (mills/net kWh) | | |
| Reagent | 2.40 | 1.79 |
| Operating Labor | 0.36 | 0.57 |
| Maintenance | 0.81 | 1.09 |
| Power | 0.39 | 0.62 |
| Total | 3.96 | 4.07 |
| Sulfur Dioxide (lb/MMBtu) | | |
| Inlet | 6.7 | 4.5 |
| Outlet | 1.2 | 1.1 |
| Collected | 5.5 | 3.4 |
| Load Factor (%) | 49 | 45 |

## SUMMARY

Modifications to operating lime double alkali systems have improved their operation. Costs have gone down and dependability up, so that the process is the most satisfactory one available for use on high sulfur coal. Other changes which are now being demonstrated will make future costs even lower.

## MODIFICATIONS TO OPERATING SYSTEMS

Since the reaction between lime and the absorbed $SO_2$ occurs in a precipitation tank that is not directly connected with the scrubber, the double alkali process offers the flexibility of design to modify the reaction variables without influencing the scrubbing operation. This flexibility has allowed significant improvements in crystal size and sludge dewatering characteristics at both the Newton and A. B. Brown stations. At start-up, both of these units experienced problems with a variable-quality filter cake and corresponding problems with cake washing efficiencies and cake handling characteristics. Consequently, studies were undertaken to improve the crystal size of the precipitated calcium salts. Both full-scale units now produce a dry, and usually non-thixotropic, filter cake resulting from relatively minor changes to the reaction tank system.

## CURRENT COST AND DEPENDABILITY

Double alkali is clearly cost competitive (4 mills/kWh operating cost), more dependable (greater than 95% available), and more efficient (capable of attaining 90% removal) on high sulfur coal applications than any other commercially demonstrated technology. The only issues clouding the future of the process have been perceptions that solids quality is suspect and reagent costs are too high. The former issue has been resolved by the success of the modifications made by CIPS and SIGECO. The latter issue has been disproved by the low actual costs experienced by users of the process.

## FUTURE IMPROVEMENTS

The cost of the double alkali process will become even lower with the imminent commercialization of limestone for regeneration in place of lime. Use of limestone is made fairly simple by the flexibility of the double alkali reaction system. Reaction tank design and chemical process variables can be altered to complete the reaction of the limestone while still providing good dewatering characteristics and without altering the scrubbing operation. Consequently, the good scrubber system availability and efficiency history of double alkali scrubbing systems can be maintained while using the lower cost limestone for regeneration of the scrubbing liquor.

In 1984 EPRI will sponsor a 3 megawatt demonstration of limestone double alkali. NIPSCO has agreed to serve as a cosponsor for the program and will be furnishing a site at Schahfer Station.

# PILOT EVALUATION OF
# LIMESTONE REGENERATED DUAL ALKALI PROCESS

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# INTRODUCTION

The sodium based dual alkali (DA) process is one of the second generation flue gas desulfurization (FGD) technologies currently utilized in the United States.(1) The DA process has the advantages of clear solution scrubbing, high $SO_2$ removal efficiency, low liquid to gas (L/G) ratio, and high reliability.(2) All existing commercial-scale DA systems use lime to react with spent scrubber effluent and regenerate the sodium sulfite scrubbing solution. Since lime is produced from limestone by an energy intensive calcination process, the direct use of limestone is increasingly more attractive with the rising cost of energy. In recent years, unit weight lime cost has been as much as 5 to 10 times the cost of limestone. It is estimated that a significant cost savings could be realized by converting a DA FGD system from lime to limestone.(3)

In order to promote the more advanced and more economical limestone DA air pollution control technology, EPA's Industrial Environmental Research Laboratory at Research Triangle Park, North Carolina (IERL-RTP, NC) has sponsored a series of research projects. Factors influencing limestone reactivity and system chemistry were identified by early laboratory work. Limestone regenerations of simulated scrubbing solutions were studied by bench-scale tests with promising results(4,5). The technical feasibility of the limestone DA process was evaluated by conducting prototype testing with the 20 MW facility at Gulf Power Company's Scholz Steam Plant.(6) Excellent $SO_2$ removal efficiencies in excess of 95 percent were achieved; limestone utilizations were also high, over 97 percent. However, the soda ash consumption of 0.29 moles of $Na_2CO_3$/mole of $SO_2$ removed far exceeded conventional consumption of 0.05 in a lime DA system.(7) Solids content in the filter cake ranged between 35 and 45 percent, which was below the anticipated 50 to 55 percent. The continuous operation was also limited by the intermittent production of very fine, needle-shaped crystalline solids with poor settleability. These fine solids did not settle in the thickener and caused interruption of system operation or system upset, when they were carried over from the thickener overflow to the absorber.

In order to support future full-scale operation and to promote system feasibility, a pilot-scale dual alkali system was established by IERL-RTP, and testing started in 1979. The pilot plant successfully simulated the prototype-scale testing at Scholz steam plant and later demonstrated the long term operability of limestone dual alkali processes.(3) Additional pilot plant tests were conducted to study factors affecting filter cake quality and soda ash consumption rate. This paper reports on the results of testing during the period February 1982 through March 1983. This recent pilot plant testing showed that significant improvement in soda ash consumption and filter cake quality could be achieved with proper system control. The causes of system upset by non-settleable solids were also identified and demonstrated in tests. The objectives of this paper are to present the highlights of recent pilot plant testing and to discuss, generally, limestone dual alkali processes.

## TEST FACILITY

The absorber is a 23 cm (9 inch) diameter tray tower designed for 8 $m^3$/min flue gas capacity (0.1 MW). The overall process flow diagram is shown in Figure 1. Flue gas from an oil/gas-fired boiler is drawn through the absorption tower by an induced draft fan located immediately upstream from the stack. Gaseous $SO_2$ from cylinders is fed into the ducting before the absorber to spike the flue gas to predetermined concentrations of $SO_2$. The oxygen content of the flue gas is controlled by adjusting the boiler excess air. The absorber contains a spray section (quench) followed by three trays in series for gas/liquid contacting. The trays are sieve-type with 4.8 mm (3/16-inch) holes on a 9.5 mm (3/8-inch) triangular spacing. Design pressure drop across the trays is 20 cm (8 inches) of water. Regenerated scrubbing liquor from the thickener hold tank is fed to the top tray and overflows a 1.3 cm (1/2-inch) weir into a collection box and then to successive trays via internal downcomers and weirs countercurrent to the flue gas flow. To prevent short-circuiting of gas around the trays, liquor from the bottom tray is collected in a weir box and overflows to the hold tank through a standpipe.

Spent scrubbing solution from the hold tank is pumped to the reactor system based on liquid level control. Slurry flows through the four reactors in series by gravity overflow. Limestone is fed to the first reactor as 40% slurry. The feedrate is manually set as required for either pH or reactant stoichiometry control. Soda ash is added to the second or the third reactor as a dry powder (for ease of operation in a small pilot unit).

Reactor effluent slurry flows by gravity to the thickener centerwell. Clarified liquor overflows from the thickener to the forward feed hold tank from which it is pumped to the absorber.

Two dewatering systems, a rotary drum filter and a belt filter, were used to evaluate the filterability of the thickener underflow slurry. The drum filter is equipped with a single stage cake washing device and the belt filter with a three-stage countercurrent washing system.

## PROCESS CHEMISTRY

The overall main reaction in a limestone regenerated DA process may be represented by:

$$CaCO_{3(s)} + SO_{2(g)} \xrightarrow{H_2O} CaSO_{3(s)} + CO_{2(g)} \qquad (1)$$

One mole of limestone reacts with 1 mole of $SO_2$ to produce 1 mole of calcium sulfite and 1 mole of carbon dioxide, according to this equation.

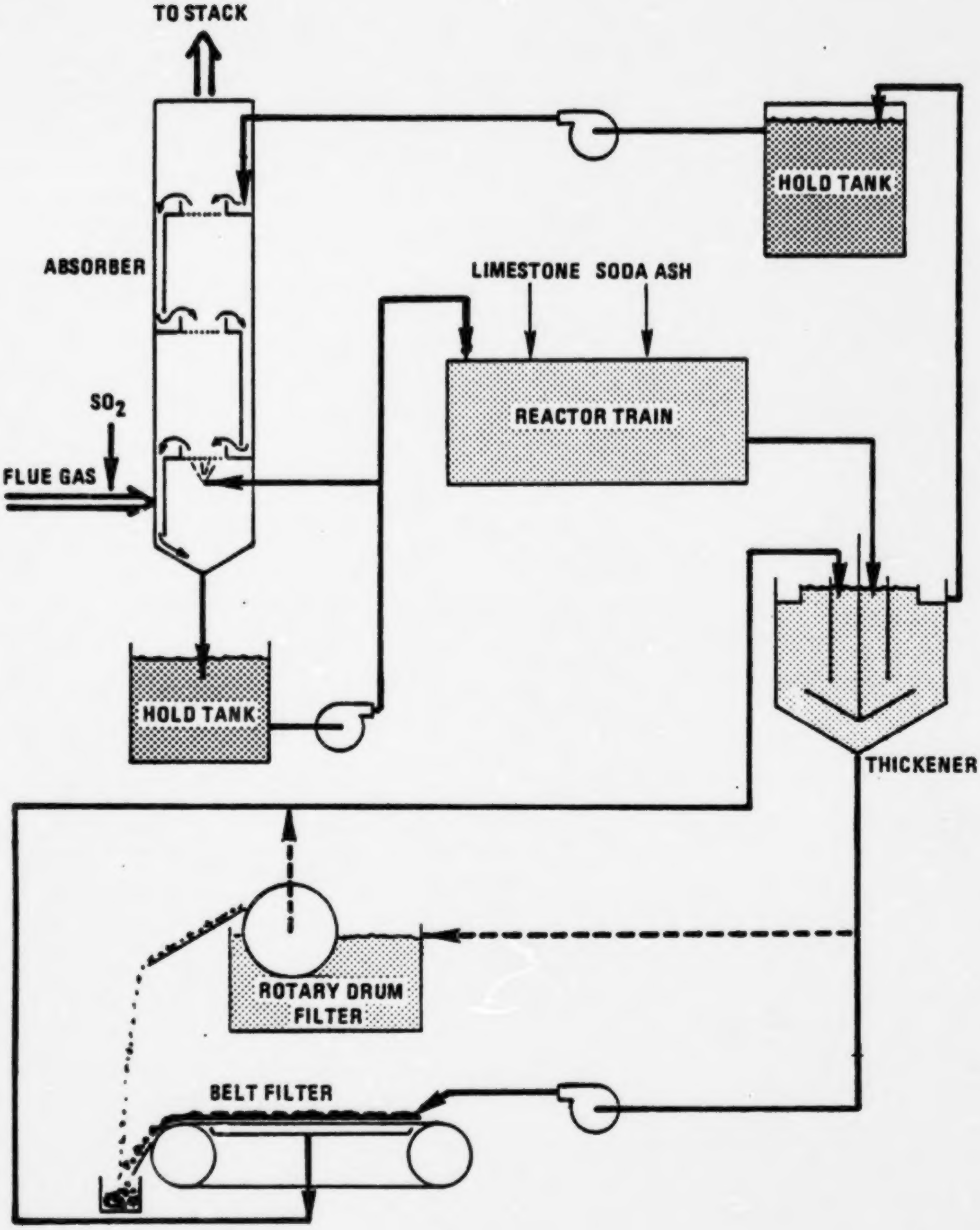

Figure 1. Flow diagram of IERL-RTP dual alkali pilot plant.

## Reactions in the Absorber

The major chemical reactions that occur in the absorber include:

### Absorption

$$SO_{2(g)} \longrightarrow SO_{2(aq)} \quad (2)$$

$$O_{2(g)} \longrightarrow O_{2(aq)} \quad (3)$$

### Desorption

$$H_2CO_{3(aq)} \longrightarrow CO_{2(aq)} + H_2O_{(1)} \quad (4)$$

### Neutralization

$$SO_3{}^{--}{}_{(aq)} + SO_{2(aq)} + H_2O_{(1)} \longrightarrow 2HSO_3{}^{-}{}_{(aq)} \quad (5)$$

$$HCO_3{}^{-}{}_{(aq)} + SO_{2(aq)} + H_2O_{(1)} \longrightarrow H_2CO_{3(aq)} + HSO_3{}^{-}{}_{(aq)} \quad (6)$$

### Oxidation

$$HSO_3{}^{-}{}_{(aq)} + 1/2\ O_{2(aq)} \longrightarrow SO_4{}^{--}{}_{(aq)} + H^{+}{}_{(aq)} \quad (7)$$

$$SO_3{}^{--}{}_{(aq)} + 1/2\ O_{2(aq)} \longrightarrow SO_4{}^{--}{}_{(aq)} \quad (8)$$

Absorption of $SO_2$ and desorption of $CO_2$ are governed by gas-liquid mass transfer and equilibria between the $SO_2$ and $CO_2$ in the flue gas and in the recirculated scrubbing liquor. If the alkaline species in the scrubbing liquor (e.g., $SO_3{}^{--}$), were reduced by low pH due to insufficient limestone stoichiometry, a drop of $SO_2$ absorption rate will result. On the other hand, higher L/G ratio and liquid holdup in the absorber can increase the $SO_2$ removal efficiency.

Neutralization of the absorbed $SO_2$ by aqueous alkaline species is dominated by the essentially instantaneous reaction between $SO_3{}^{--}$ and hydrated $SO_2$. Oxidation of the sulfite species to sulfate ion is accompanied by the absorption of oxygen in the flue gas. The oxidation reaction occurs predominantly in the absorber. However, any contact between oxygen (from air or flue gas) and aqueous sulfite or bisulfite will result in oxidation.

## Reactions in the Reactors

The primary chemical reactions that occur in the reactors include:

### Dissolution and Desorption

$$CaCO_{3(s)} + HSO_3^-{}_{(aq)} \longrightarrow Ca^{++}{}_{(aq)} + SO_3^{--}{}_{(aq)} + HCO_3^-{}_{(aq)} \quad (9)$$

$$HCO_3^-{}_{(aq)} + HSO_3^-{}_{(aq)} \longrightarrow H_2CO_{3(aq)} + SO_3^{--}{}_{(aq)} \quad (10)$$

$$H_2CO_{3(aq)} \longrightarrow CO_{2(g)} + H_2O_{(1)} \quad (11)$$

### Precipitation

$$Ca^{++}{}_{(aq)} + (1-x)SO_3^{--}{}_{(aq)} + xSO_4^{--}{}_{(aq)} + yH_2O_{(1)} \longrightarrow Ca(SO_3)_{1-x}(SO_4)_x \cdot yH_2O_{(s)} \quad (12)$$

Limestone is dissolved in the reactors to replenish the aqueous alkaline species which are consumed by the neutralization reaction in the absorber. Most of the carbon dioxide resulting from limestone dissolution evolves to the atmosphere from the reactor surface. The system product is a solid solution, $Ca(SO_3)_{1-x}(SO_4)_x \cdot yH_2O$, where x is proportional to the oxidation level and ranges up to about 0.2. Limestone utilization is defined as:

$$\text{Percent utilization} = 100 \times TS/TCa = 100/\text{stoichiometric ratio} \quad (13)$$

where TS: total sulfur in the product solids, moles
TCa: total calcium in the product solids, moles

Precipitation of solids occurs in accordance with the solubility product, $K_{sp}$, which is taken here to be equal to(8):

$$K_{sp} = a_{Ca^{++}} \cdot a_{SO_3^{--}} = 4.5 \times 10^{-7}\ (\text{mole/liter})^{-2} \text{ at } 50°C \quad (14)$$

where $a_{Ca^{++}}$ and $a_{SO_3^{--}}$ are calcium and sulfite ion activities, respectively.

Since the sulfite ion concentration in the scrubbing liquor is usually maintained in the range of 0.1 to 0.5 M, the calcium ion concentration is extremely low; i.e., sodium is the dominant cation in the scrubbing liquor. Due to the low solubility, most of the carbon dioxide produced by the dissolution of limestone evolves almost immediately into the atmosphere. The concentration of carbonate species (<0.05M) in the absorbent liquor is usually orders of magnitude lower than that of sulfite species.

The process chemical conditions can be reflected by two important concentration ratios, sulfite to bisulfite and sulfate to sulfite. The sulfite to bisulfite molar ratio and the pH are interdependent and can be adjusted by limestone stoichiometry. The sulfate to sulfite molar ratio is determined by the balance of oxidation and coprecipitation rates. The absolute concentration of all species is reflected by the total sodium concentration, which is controlled by $Na_2CO_3$ addition.

## RESULTS AND DISCUSSION

Pilot plant tests have been performed over the range of operating conditions indicated in Table 1. The results demonstrate that solids with reasonably good dewatering properties can be produced over a range of simulated utility boiler operating conditions. Soda ash consumption rate substantially lower than that in previous test programs can be achieved by improved filter cake washing. System upset simulation tests were conducted to identify the causes of system upset. It was demonstrated that system upset could be avoided by proper design and control of the processes. The pilot plant has been operated successfully for more than 10 months over the wide range of operating conditions shown in Table 1 without any system upset. The various aspects of system performance are discussed below.

### $SO_2$ Removal

Over 92% $SO_2$ removal efficiency was readily achieved at 3000 ppm flue gas $SO_2$ concentration. The two $SO_2$ monitoring techniques, ultraviolet and wet gas analysis, were in good agreement. The $SO_2$ removal efficiency was a function of system pH, sulfite ion concentration, and absorber internals. Material balance indicated that the absorber "make-per-pass" (moles of $SO_2$ absorbed per liter of absorbent flowing in the absorber) was in the range of 0.1 to 0.13 mole of $SO_2$ per liter of scrubbing solution, which was an order of magnitude higher than that of slurry scrubbing processes. The high make-per-pass of the pilot limestone dual alkali absorber was reflected by the low L/G ratios (0.8-1.2 $l/m^3$ or 6-9 gal/1000 acf utilized), as shown in Table 2, compared with the high L/G (5.3-9.3 $l/m^3$ or 40-70 gal/1000 acf, usually) of slurry scrubbing processes.(9)

### Limestone Utilization

High calcium, Fredonia limestone was utilized to regenerate the scrubbing liquor in all testing described herein. The chemical composition and particle size distribution are shown in Tables 2 and 3. In previous testing, simulating conditions at the Gulf Power Scholz plant, Sylacauga limestone was also tested in certain runs and proved to be acceptable.

As shown by Equation 9, bisulfite ion is the predominant acidic species which reacts with the limestone and dissolves it. Figure 2 illustrates the effect of acidity concentration on limestone utilization obtained from the pilot plant tests with the pH of regenerated liquor between 6.4 and 6.5.

Table 1. Operating Ranges of Limestone Dual Alkali Pilot Plant Tests

| | |
|---|---|
| L/G ratio, $l/m^3$: | 0.80-1.2 (6-9 gal/1000 acf) |
| Limestone stoichiometry: | 1.0-1.2 |
| Scrubber feed pH: | 6.0-6.8 |
| Scrubber effluent pH: | 5.4-6.3 |
| Active sodium concentration[a], M: | 0.48-1.5 |
| TOS, M | 0.34-1.1 |
| Flue gas $O_2$, % | 5-10 |
| Sulfate to sulfite molar ratio: | 1.4-3.9 |
| Oxidation, %: | 6-20 |

[a] Active sodium is defined as $2[SO_3^{--}] + 2[CO_3^{--}] + [HCO_3^-] + [HSO_3^-]$ expressed as $Na^+$ concentration. Active sodium is actually a misnomer since $Na^+$ does not participate in any of the dual alkali reactions but is used for convenience.

Table 2. Chemical Composition of the Limestone Used for Dual Alkali Pilot Plant Testing

| | | Chemical Composition, wt. percent | | | |
|---|---|---|---|---|---|
| Limestone | Location of Quarry | Calcium (Ca) | Magnesium (Mg) | Carbonate ($CO_3$) | Acid Insolubles |
| Fredonia | Fredonia, Kentucky | 35.8 | 2.5 | 60.5 | 2.2 |

Table 3. Results of Wet Sieve Analysis of Limestone Used for Dual Alkali Pilot Plant Testing

| | Weight Percent | | | | |
|---|---|---|---|---|---|
| Limestone | -325 mesh | -230 mesh | -200 mesh | -170 mesh | -100 mesh |
| Fredonia | 79.6 | 89.1 | 91.8 | 98.4 | 99.2 |

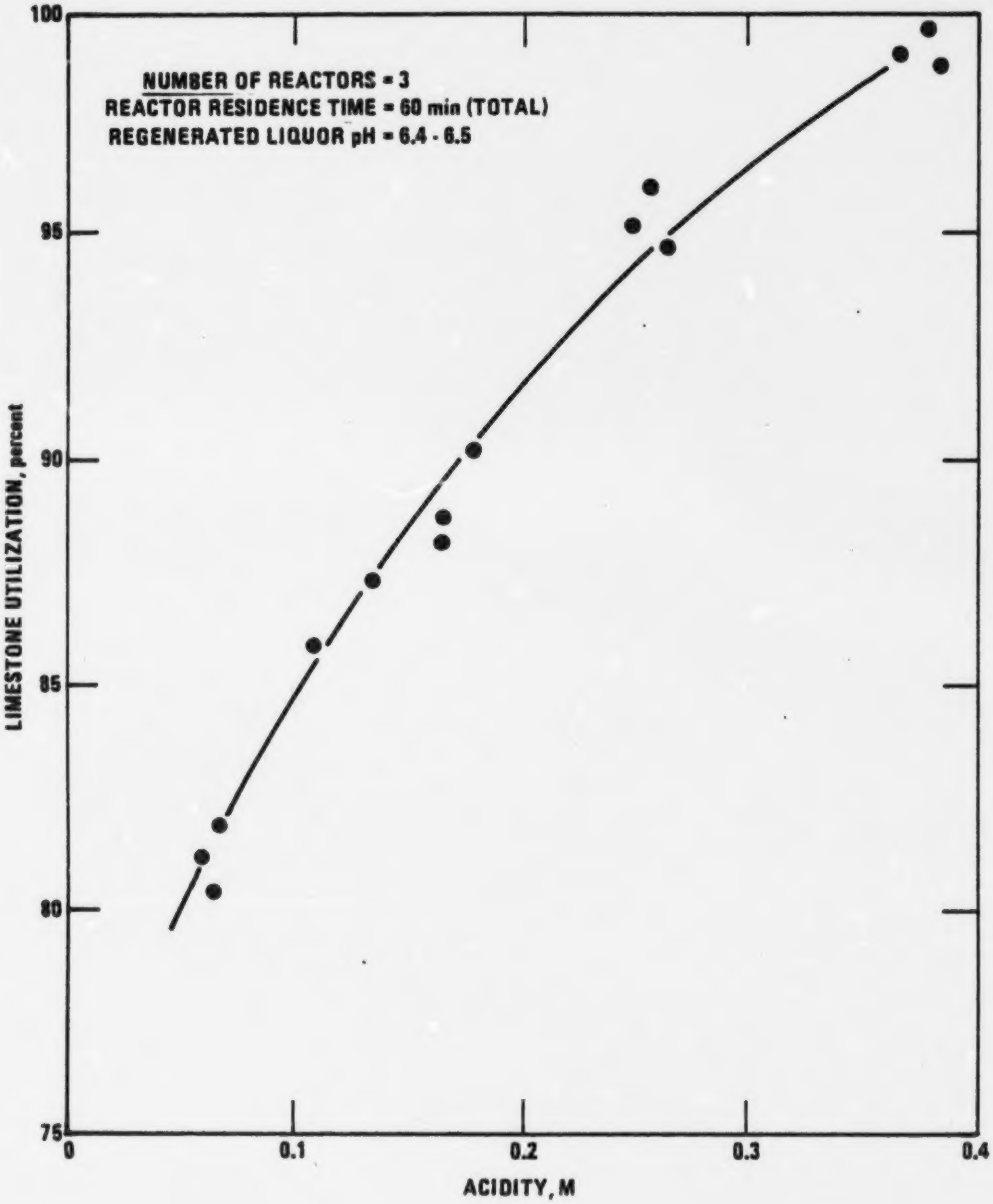

Figure 2. Effect of (thymolphthalein) acidity on limestone utilization.

(Acidity in a DA system is defined as the concentration of all acid species determined by titrating a quantity of solution with standard base to the thymolphthalein end point of pH 10.6.) A minimum concentration of acidity at 0.2 M was needed to attain 90% limestone utilization. When the acidity concentration was above 0.4 M, 95-100% limestone utilization could be achieved. Since the acidity concentration of a concentrated mode DA process is usually higher than 0.2 M, it was concluded that high limestone utilization (greater than 90%) could be obtained in the DA process under normal operating conditions.

## Oxidation and Sulfate Balance

Two effects of oxidation were observed during the pilot plant tests, sulfate ion accumulation and solids quality deterioration. The latter will be discussed in the next section. The level of sulfate ion accumulation is determined by the oxidation rate and sulfate removal rate. Sulfate ion can leave the system either in liquids, wetting the waste product as sodium sulfate, or in solids as calcium sulfite/sulfate crystals. The latter is more desirable because sodium is not lost, and the waste cake will contain less soluble salts which can be leached into the ground water near a disposal site. Calcium sulfate is coprecipitated with calcium sulfite in the reactors to form a "solid solution" as indicated by Equation 12. (The liquid phase calcium and sulfate concentrations never exceed the gypsum solubility product, and no pure gypsum phase forms.) The relationship between sulfate/sulfite molar ratio in the liquid and in the precipitated solids is shown in Figure 3. Overall, the pilot plant sulfate balance showed that the DA system was capable of keeping up with oxidation rates up to 20% of the $SO_2$ removed--oxidation rates higher than those anticipated for most medium- and high-sulfur coal applications. (An oxidation rate of 20% is equivalent to a $SO_4^{--}/SO_3^{--}$ molar ratio of 0.25 in the solids.) In other words, sulfate balance can be accomplished by calcium sulfite/sulfate coprecipitation with closed-loop operation for the medium- to high-sulfur coal applications of the limestone DA processes.

Oxidation is an important but undesirable side reaction in DA processes since high oxidation could convert the useful total oxidizable sulfur (TOS, moles of sulfite ion plus bisulfite ion per liter of solution) species to inert sulfate ion and deteriorate solids qualities. Efforts have been made to characterize the oxidation reaction and to minimize its rate.

Short term (8 to 12 hours each run) pilot plant tests were performed by recirculating $Na_2SO_3/NaHSO_3$ solution around the absorber which was isolated from the rest of the system. Oxidation tests were conducted at 3.5, 5.5, and 8.5% flue gas oxygen concentrations. The initial TOS concentration was set at 0.3 to 0.4 M and the solution pH at about 6.7. The oxidation rate increased from 2.35 to 3.08 gmole/hr as the oxygen concentration was raised from 3.5 to 5.5%. Oxidation rate at 3.77 gmole/hr was obtained with 8.5% flue gas oxygen. It was concluded that the oxidation rate in the DA absorber is a function of flue gas oxygen concentration.

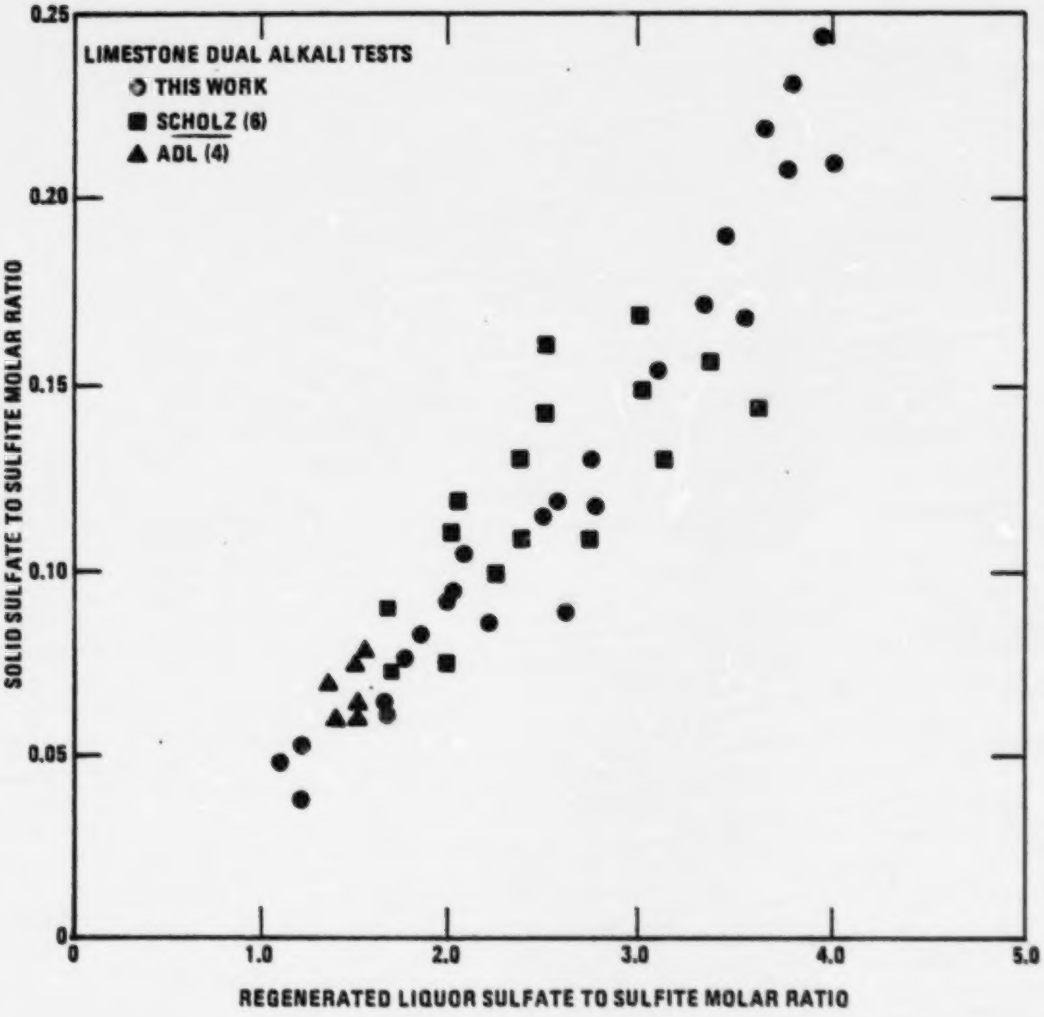

Figure 3. Ratio of sulfate to sulfite in solids as a function of sulfate to sulfite ratio in regenerated liquor.

The effectiveness of sodium thiosulfate as an oxidation inhibitor was also evaluated by pilot plant testing. It was suggested that the thiosulfate ion might act as a radical scavenger to deactivate the radicals that promoted the oxidation of sulfite and/or bisulfite ions. Results shown in Figure 4 indicate that the concentration ratio of thiosulfate ion to TOS was an important factor determining the effectiveness of sodium thiosulfate as an oxidation inhibitor. Insignificant effect was observed when the thiosulfate to TOS ratio was below 0.1. If 50% reduction of the oxidation rate is desirable, the thiosulfate to TOS ratio must be maintained at 0.5 or above, under conditions tested.

general, the action of thiosulfate as an oxidation inhibitor may be dependent upon the ratio of thiosulfate to TOS as shown in Figure 4. Since the TOS concentrations in DA systems are orders of magnitude higher than in limestone slurry scrubbing systems, a much higher concentration of thiosulfate may be required in DA systems. In limestone slurry scrubbing only a few hundred ppm of thiosulfate was reported to be effective for oxidation inhibition. However, for a concentrated sodium based limestone DA process, the TOS concentration is expected to be in the range of 0.7 to 1.0 M. Therefore, a significant amount of sodium thiosulfate would be required to cut the oxidation rate by 50%. The feasibility of using sodium thiosulfate as an oxidation inhibitor will be determined by economic trade-offs and other site specific factors.

## Filter Cake Quality

Probably the most significant impact of oxidation on system performance observed during the pilot plant tests was the change in filter cake quality. As shown in Figure 5, the % insoluble solids in the filter cake dropped with the increase of oxidation rate reflected by the sulfate to sulfite molar ratio in the regenerated liquor. When the sulfate to sulfite molar ratio was below 1.5, filter cake % insoluble solids reached 60%. The % insoluble solids in the filter cake varied inversely with the sulfate to sulfite molar ratio, reaching about 35% at a sulfate to sulfite molar ratio of 4. Operation under these conditions was considered to be undesirable because of the poor physical properties of the waste and the high losses of sodium compounds.

Coulter counter analyses were conducted to measure the particle size distribution in the reactor effluent at various sulfate to sulfite molar ratios. However, no significant changes in particle size distribution were obtained, and the mean particle diameter remained at about 20 um even though the filter cake % insoluble solids content dropped from 60 to 35 percent. The product solids were further examined under a scanning electron microscope (SEM to observe the detailed morphology of the individual solid particles. As can be seen in the SEM photomicrographs reproduced in Figures 6 and 7, the two product solids were physically different. The photomicrographs shown in Figure 6 were taken at a magnification of 1000x. The solid "particles" shown in Figure 6 were actually clusters composed of agglomerates of crystals. The "particles" which gave 60% solids filter cake were composed of thicker, larger, and better defined crystals or platelets. However, the 35% filter cake "particles" were agglomerates of thinner, smaller, more needle-like crystals. The differences in crystal thickness were illustrated clearly by the 5000x magnification photomicrographs

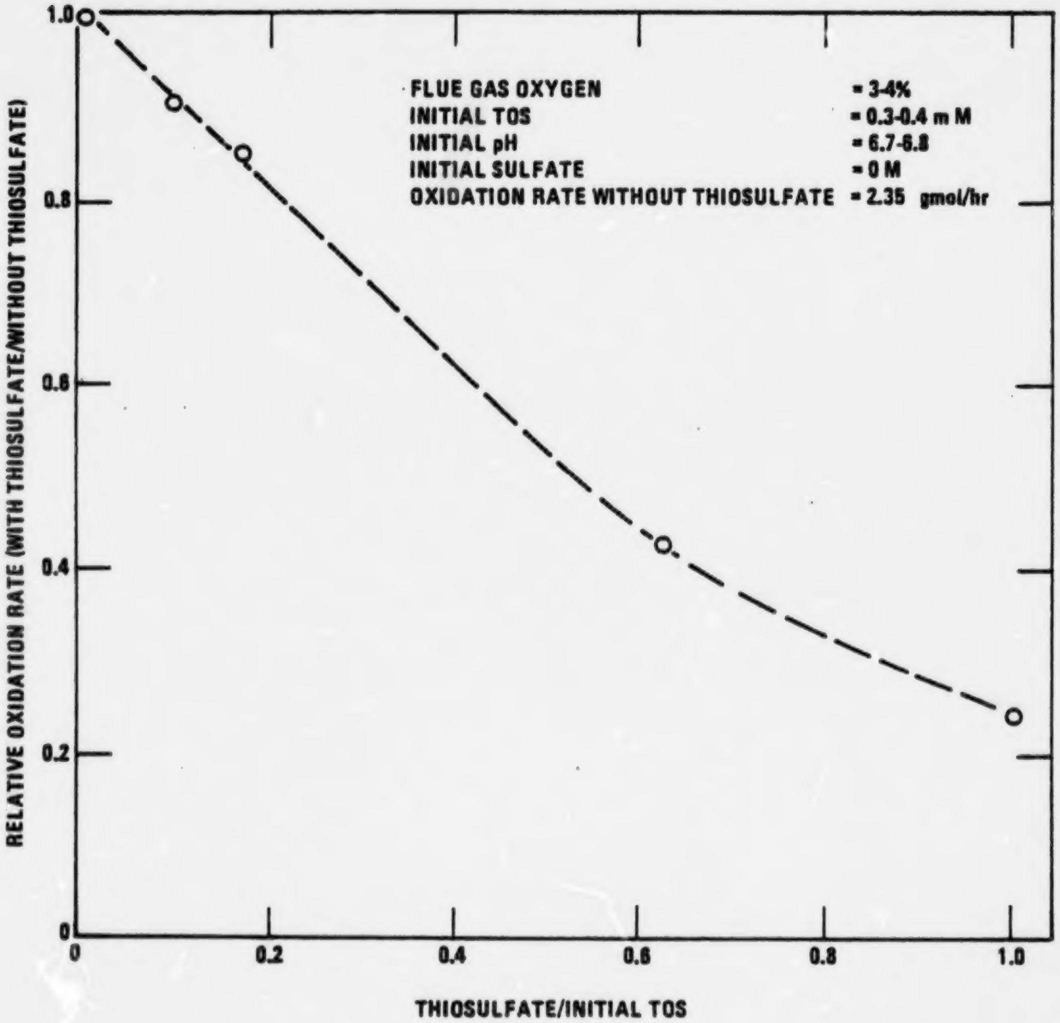

Figure 4. Effectiveness of sodium thiosulfate as an oxidation inhibitor.

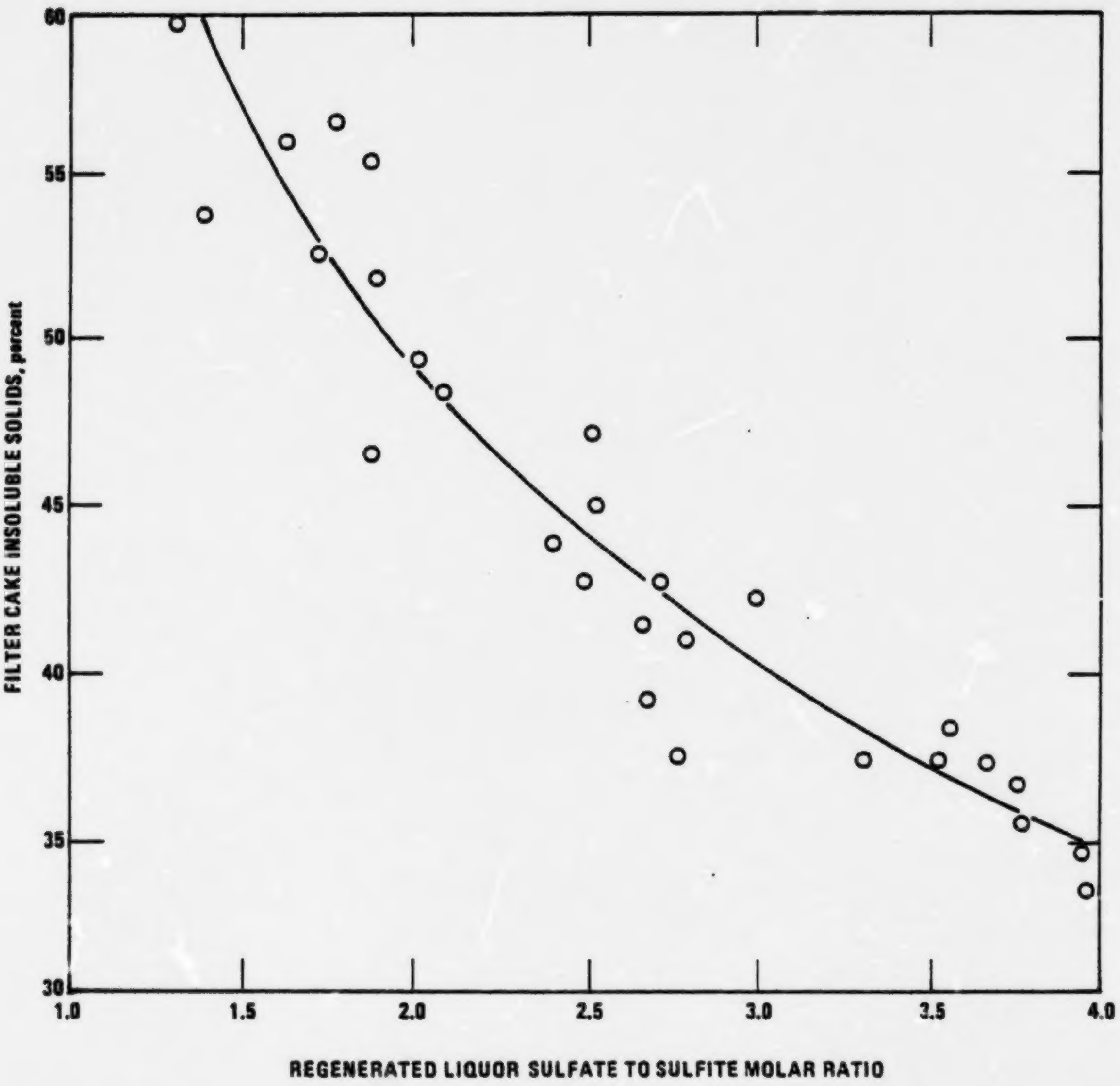

Figure 5. Percent filter cake solids as a function of sulfate to sulfite ratio in the regenerated scrubbing liquor.

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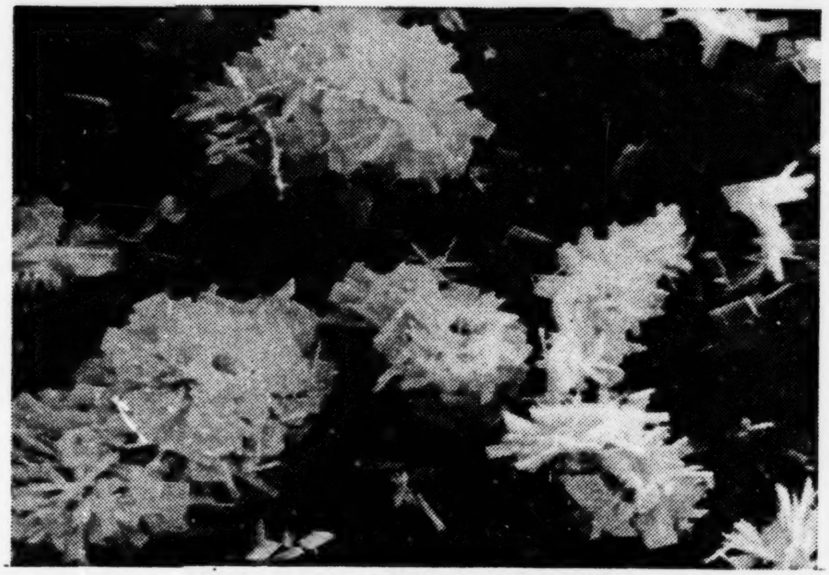
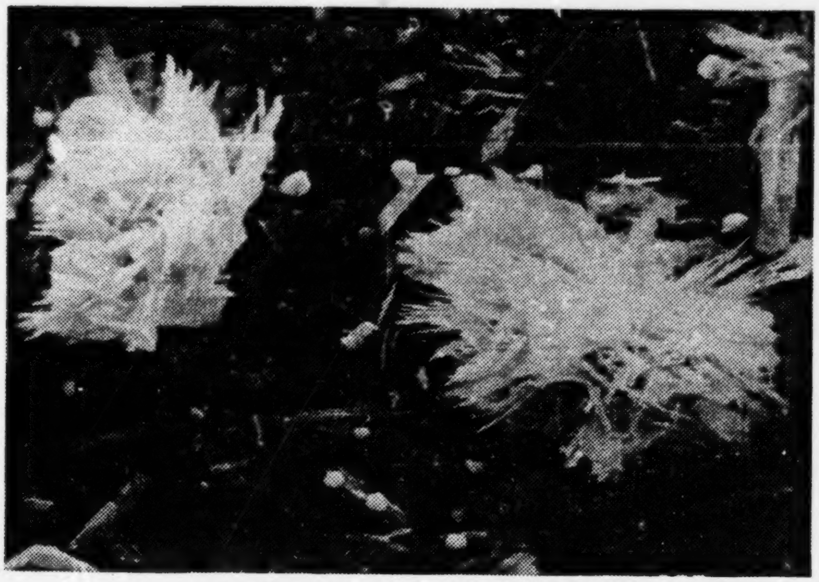
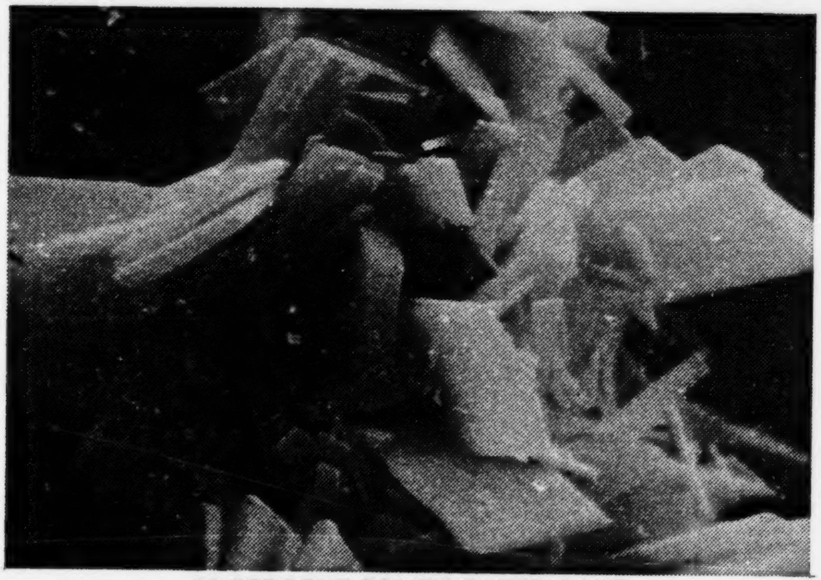


60 PERCENT SOLIDS FILTER CAKE

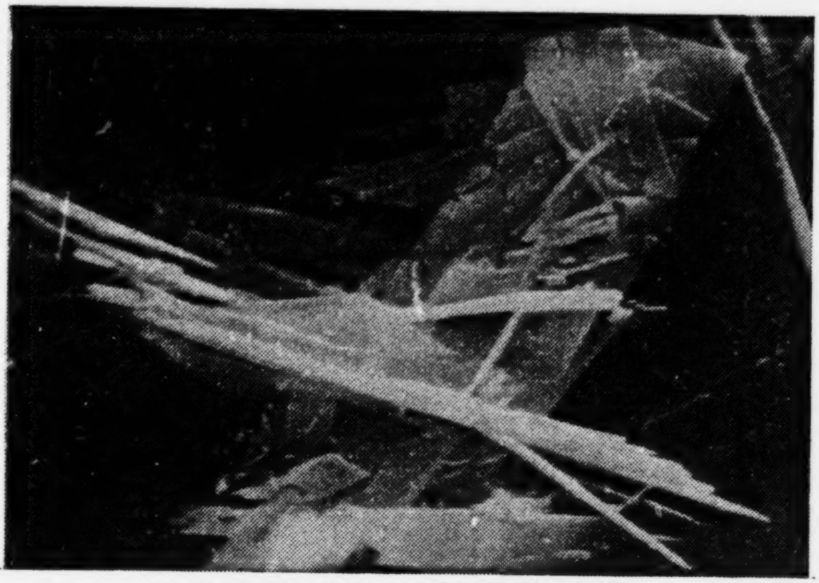


35 PERCENT SOLIDS FILTER CAKE

Figure 6. Limestone dual alkali solid product (1000x).



60 PERCENT SOLIDS FILTER CAKE



35 PERCENT SOLIDS FILTER CAKE

Figure 7. Limestone dual alkali solid product (5000x).

in Figure 7. An interpretation of Figure 7 is that crystal fractures (which might be caused by the collision of agitator blades) and thin platelets or needles in reactors were observed with 35% filter cake "particles" at high sulfate to sulfite molar ratio; and that these fine particles were responsible for the poor physical properties of the filter cake. It may also be postulated that the coprecipitated sulfate ion acts as an impurity which inhibits crystal growth and causes crystal defects.

## High Active Sodium vs. Low Active Sodium

In order to evaluate the effects of operating conditions on system performances such as oxidation rate and filter cake % insoluble solids, long term demonstration tests were performed at high (1.2 M) and low (0.48 M) active sodium concentrations. The operating conditions for each run are shown in Figures 8 and 9, respectively. Results summarized in Table 4 indicate that at high active sodium the sulfate to sulfite molar ratio was 1.9 which was considerably lower than the 3.9 obtained from low active sodium test. Filter cake analyses also indicate that the 8% oxidation level at high active sodium was considerably lower than the 18% observed at low active sodium. The lower sulfate to sulfite molar ratio and oxidation rate at high active sodium are reflected by the higher filter cake % insoluble solids as shown in Table 4. The decrease of oxidation rate with the increase of active sodium concentration is probably due to the ionic strength effect. As shown in Table 4, the high active sodium mode was operated with 4.5 M ionic strength which is 100% higher than that of low active sodium. Data in the literature indicate that both the solubility and diffusivity of oxygen in aqueous solutions can be reduced by higher ionic strength through the change of liquid viscosity. As a result, the mass transfer rate of oxygen from flue gas to scrubbing solution is reduced, and the liquid-phase oxidation rate is also decreased.

## Soda Ash Consumption

With a properly designed and operated system, the majority of the sodium loss should occur with the liquor entrained in the filter cake. Sodium ion concentration in the scrubbing liquor, filter cake % insoluble solids, and filter cake wash efficiency are the three major factors determining the rate of sodium consumption. The typical sodium ion concentration of a limestone DA process is expected to be in the range of 2 to 3 M. As shown in Figure 10, the soda ash consumption will be significant if there is no filter cake washing to recover the sodium species, especially when the filter cake % insoluble solids is below 50%. However, the soda ash consumption can be reduced substantially by filter cake washing with a reasonable wash efficiency. The filter cake wash efficiency was defined as:

$$\text{washing efficiency} = \left(1 - \frac{\text{sodium content after washing}}{\text{sodium content before washing}}\right) \times 100\% \quad (15)$$

A rotary drum filter with single stage washing was first used to evaluate the washability of sodium compounds from the filter cake. Only 10 to 20% wash efficiency was obtained. The poor wash efficiency was attributed to filter cloth blinding or poor filter design. Most of the wash water did not penetrate the cake and just flowed down off the filter cake surface.

**SCRUBBER FEED LIQUOR**

| | |
|---|---|
| TOTAL SULFUR | 1.65 M |
| TOTAL OXIDIZABLE SULFUR | 0.70 M |
| TOTAL ALKALINITY | 0.50 M |
| TOTAL SODIUM | 3.00 M |
| pH | 6.60 |

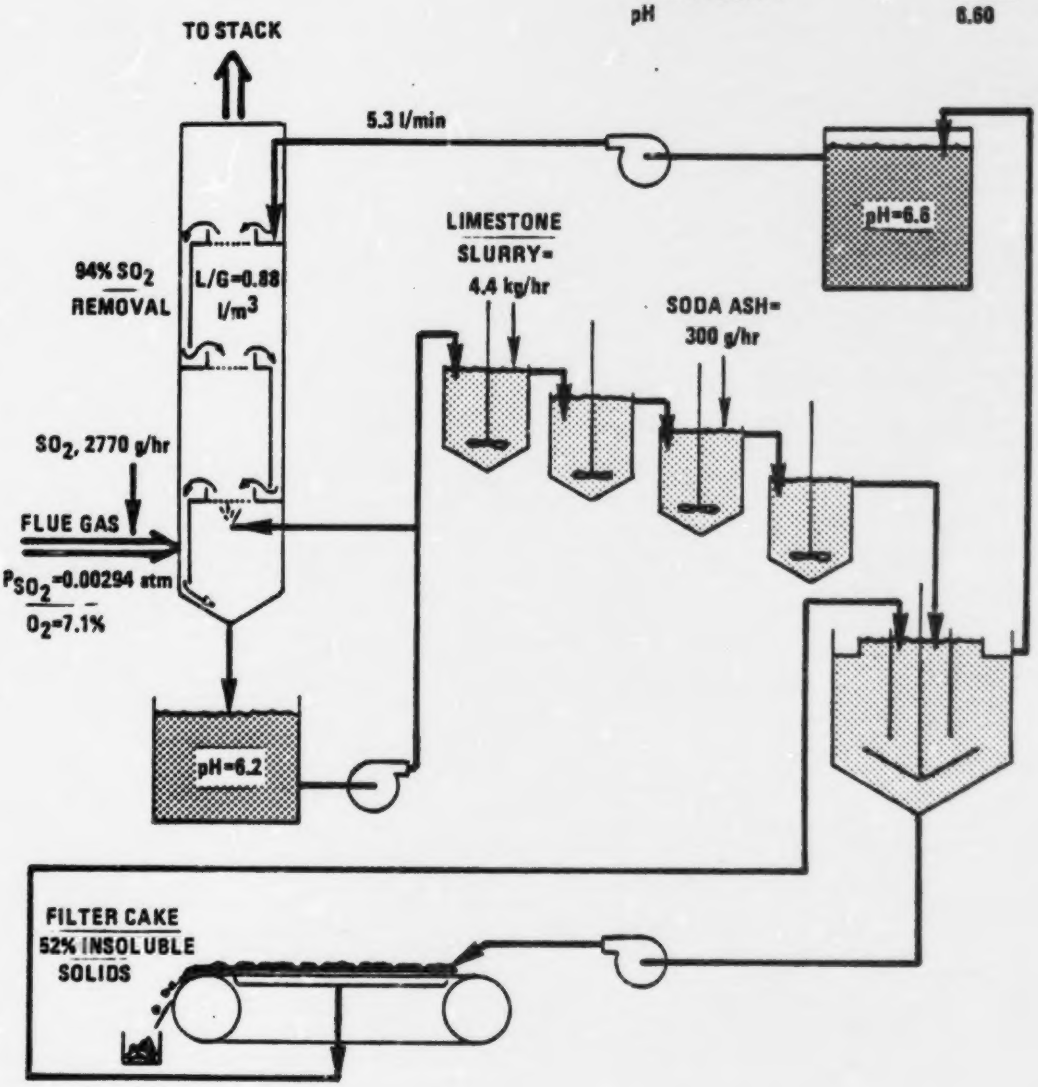


Figure 8. Operating conditions of high active sodium (1.2 M) test.

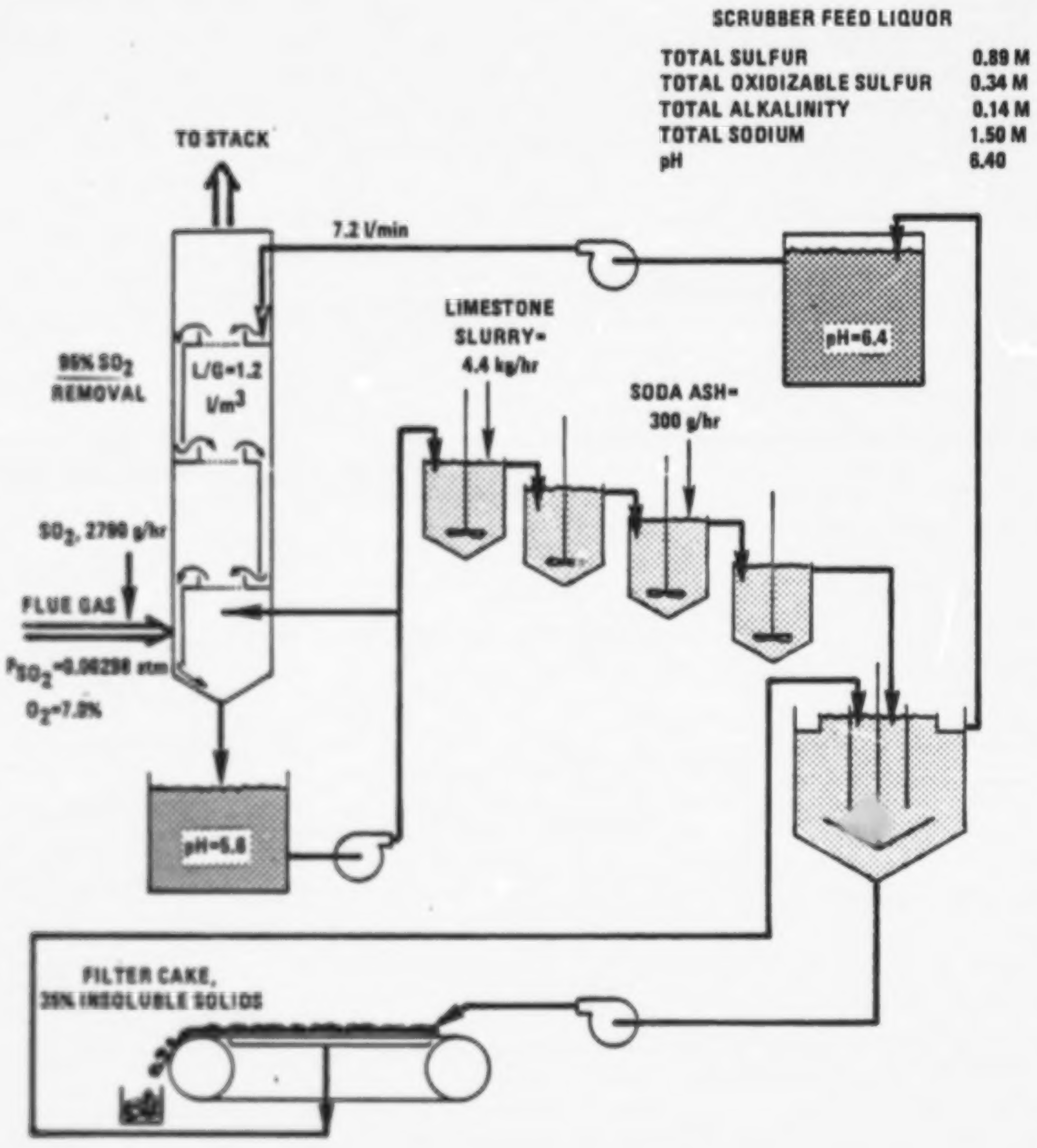


Figure 9. Operating conditions of low active sodium (0.48 M) test.

In an effort to reduce sodium losses by improving wash efficiency, a belt filter with three stages of countercurrent washing was installed and then evaluated. Three sets of filter cake washing tests were conducted. The results, compared with wash efficiencies predicted by a wash model, are shown in Figure 11. The wash efficiency, assuming countercurrent washing with complete mixing of wash water and occluded liquor at each stage, can be calculated by this model as follows:

$$\text{wash efficiency} = \left(1 - \frac{R - 1}{R^{n+1} - 1}\right) \times 100\% \text{ where } R>1 \qquad (16)$$

where R is the number of filter cake water displacements, and n is the number of washing stages.

Table 4. The Effects of Active Sodium and Ionic Strength on Oxidation and Resulting Filter Cake Quality at the IERL-RTP Dual Alkali Pilot Plant

| | High Active Sodium Mode | Low Active Sodium Mode |
|---|---|---|
| Active sodium, M | 1.2 | 0.48 |
| Total sodium, M | 3.0 | 1.5 |
| Ionic strength, M | 4.5 | 2.25 |
| Sulfate/sulfite molar ratio(a) | 1.9 | 3.9 |
| Oxidation rate(b), % | 8 | 18 |
| Filter cake insoluble solids, % | 52 | 35 |
| Flue Gas $O_2$, % | 7.1 | 7.0 |

(a)in regenerated liquor
(b)based on filter cake analyses

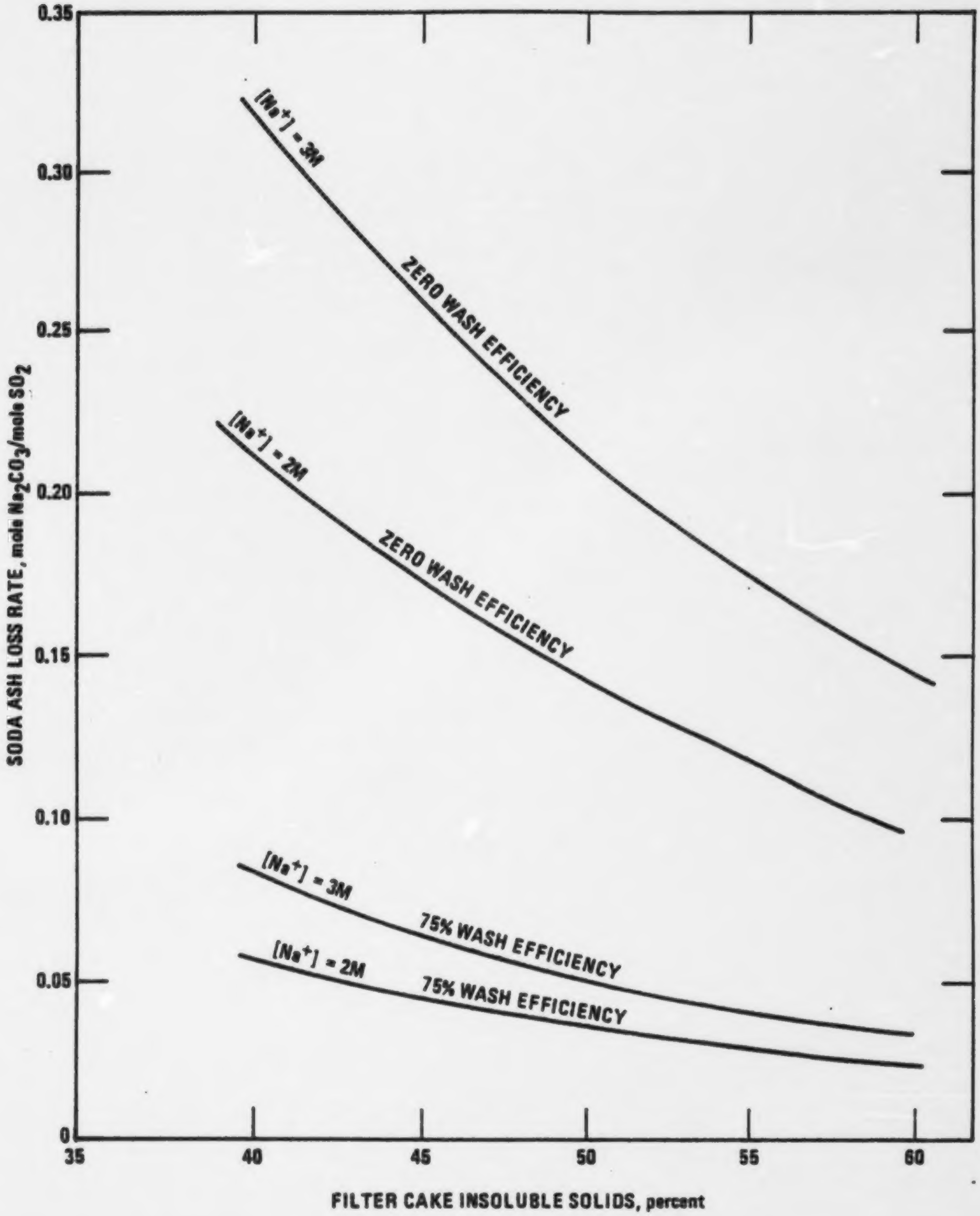


Figure 10. Soda ash loss rate through unwashed filter cake as a function of filter cake insoluble solids and scrubbing liquor sodium concentrations.

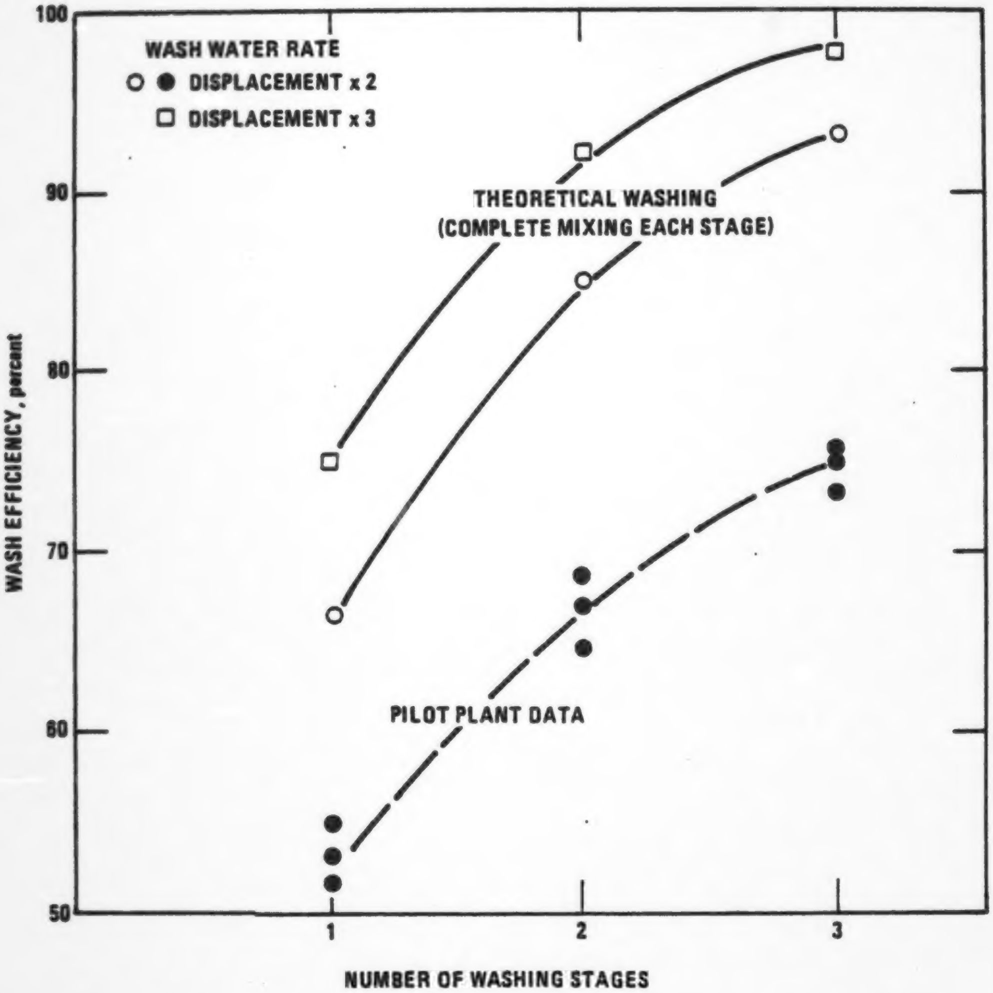


Figure 11. Performance of belt filter with countercurrent washing.

Figure 11 shows that wash efficiencies lower than those predicted by the model were obtained from the pilot plant. With two filter cake water displacements and three washing stages, approximately 75% wash efficiency was observed, which is 18.3 percentage points lower than the predicted 93.3% wash efficiency. There are two reasons for the difference. First, the wash model assumes that all sodium species are washable. However, data indicated that about 10 to 15% of the sodium species are not washable. Coprecipitation and crystal occlusion might explain why some of the sodium species contained in the filter cake cannot be washed out. Secondly, the model assumes an even distribution and complete mixing of wash water with the entrained cake liquor. However, cake cracking causes some bypassing or channeling of wash water and results in less than ideal mixing conditions.

The model indicates that the filter cake washing efficiency could be maximized by further increasing the quantity of wash water and/or the number of washing stages. Two displacements of wash water were used in these tests since that was the volume of wash water permitted by material balance when limestone was added to the DA reactors as 40% slurry (limestone in fresh water). Material balance indicates that if limestone is fed as a dry powder, the wash rate can be increased to three displacements, corresponding to an ideal wash efficiency of 97.5%.

Pilot plant data indicated that the average filter cake insoluble solids was about 52% at 3M total sodium concentration (Table 4). Figure 10 indicated that the soda ash requirement to replenish the sodium loss with unwashed filter cake should be about 0.2 mole $Na_2CO_3$ per mole of $SO_2$ absorbed. If 75% filter cake wash efficiency is achieved, the soda ash consumption rate is predicted to be as low as 0.05 mole $Na_2CO_3$ per mole of $SO_2$ absorbed.

## Simulation of System Upsets

System upsets are characterized by non-settling finely divided solids suspended throughout the liquid in the system. The thickener cannot produce clear regenerated liquor overflow to feed the absorber, and the system ceases to function as a dual alkali process.

Pilot plant testing indicated that system upsets may be caused either mechanically or chemically. Mechanical attrition of crystals produced poor quality, non-settleable solids.(3,10) System upset was also observed to be purely a function of chemistry; specifically, it would occur with sulfate to sulfite molar ratios above about 4.

A mechanically caused upset was demonstrated by using the reactor design shown in Figure 12a, which included long baffles and the agitators pumping downward.* This design produced a quiescent zone between the baffles and the

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*It has been reported by FMC Corporation that they experienced, if anything, superior performance with down draft agitation. Due to the difference in results cited by FMC Corporation and those of our pilot plant tests, and personal correspondence with Dr. R. R. Lunt, an investigator of this technology, it is clear that reactor design plays a major role in the operation of the system. It is also clear that this effect is not completely understood. We have reported the results of operation in this 0.1 MW pilot unit, and have merely tried to explain the observed results. The design of our current reactor system, however, is probably not optimal.

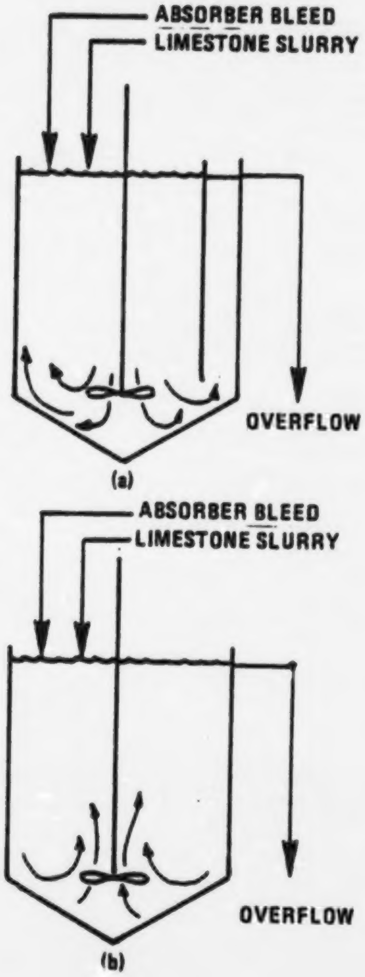

Figure 12. Reactor flow patterns utilized for system upset simulation tests.

wall of the tank. Large crystals tended to settle in the quiescent zone and accumulate in the reactors. As crystals were accumulating, the reactor solids concentration increased and the filter cake quality deteriorated. It was suspected that the increase of solids concentration favored crystal attrition, and the attrition produced extremely fine particles. Eventually, the overload of fine solids overflowed to the thickener and produced a system upset. Solids quality was improved by using the continuous stirred tank reactors with agitators pumping upward as shown in Figure 12b. When the reactor solids concentration was 3% or below, the solids settling rate reached 1.5 to 2 cm/min vs. the 0.1 cm/min during upset conditions.

A chemical upset was produced by decreasing the soda ash make-up rate to zero to let the sulfate to sulfite molar ratio increase. The solids qualities, including solids settling rate and filter cake % insoluble solids, deteriorated with the increase of sulfate to sulfite molar ratio. System upset occurred when sulfate to sulfite molar ratio reached 4.3. Heavy doses of soda ash were then added to the reactors in an attempt to reduce the sulfate to sulfite molar ratio and to reverse the system upset. The sulfate to sulfite molar ratio decreased gradually with associated improvement in solids qualities. When the sulfate to sulfite molar ratio decreased below 1.5, the solids settling rate reached 2.5 cm/min, and filter cake insoluble solids content reached 60%. This indicated that the chemical upset was reversible by adjusting the system chemistry.

## CONCLUSIONS

The following conclusions were drawn from the pilot plant studies:

1. The results confirmed that limestone dual alkali processes can provide the advantages of clear solution scrubbing with high $SO_2$ removal efficiency at low L/G and high limestone utilization.

2. The level of oxidation can be reduced by increasing the ionic strength in scrubbing solutions. The removal of the oxidation product, sulfate ion, can be accomplished by calcium sulfite/sulfate coprecipitation as solid solution with closed-loop operation and filter cake washing for medium- and high-sulfur coal applications.

3. The filter cake quality was affected by levels of oxidation or liquid phase sulfate to sulfite molar ratios. Pilot plant tests demonstrated that filter cake % insoluble solids can be improved from 35% to 52% by increasing the active sodium concentration from 0.48 M to 1.2 M to reduce the oxidation level and sulfate to sulfite molar ratio.

4. The soda ash consumption rate was influenced by scrubbing solution sodium concentration, filter cake quality, and cake wash efficiency. Pilot results achieved cake wash efficiency of 75% using three stages of countercurrent washing. Material balance projected that a soda ash consumption of 0.05 mole $Na_2CO_3$ per mole $SO_2$ removed should be attainable with closed-loop operation and 75% cake wash efficiency.

5. System upsets assumed to be caused by mechanical crystal attrition may be avoided by better design and operation of reactors, agitators and pumps. Chemically induced system upset caused by high sulfate to sulfite molar ratio is reversible and can be avoided by controlling the system chemistry in medium- and high- sulfur coal applications with normal levels of oxygen in the flue gas.

## Future EPA Test Program

The EPA/IERL-RTP test program with limestone dual alkali FGD systems is continuing. The following activities are either proceeding or planned for 1984.

- Tests evaluating the magnesium ion effects on system performance
- Tests evaluating the chloride ion effects on system performance
- Limestone type and grind tests
- Optimization of reactor design and operation
- Factorial tests to develop the interrelationship of system performance and operating parameters and to optimize the process design.

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## SESSION 6: FLUE GAS TREATMENT (COMBINED $SO_x$/$NO_x$)

Chairman: J. David Mobley
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC

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# STATUS OF THE DOE FLUE GAS CLEANUP PROGRAM

by: John E. Williams
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Pittsburgh Energy Technology Center
U. S. Department of Energy
Pittsburgh, PA 15236

## ABSTRACT

The U. S. Department of Energy directs a substantial R&D effort to develop advanced environmental control technology for coal-fired stationary sources. The Flue Gas Cleanup Program is aimed primarily at post-combustion cleanup of $SO_2$ and $NO_x$; a small part of the program is directed at characterization and improved control of respirable particulates. The programmatic goal established at Fossil Energy Headquarters is the development of technology options for 90% removal of both $SO_2$ and $NO_x$ while controlling particulates to the New Source Performance Standards (NSPS). Emphasis is placed on developing process concepts that offer potential cost reductions of 20% to 25%, compared to commercially available technology (Selective Catalytic Reduction of $NO_x$ followed by a wet limestone scrubber and the necessary baghouse or electrostatic precipitator (ESP)). The commercialization or application period is expected to be in the late 1980's or early 1990's.

The Flue Gas Cleanup Program is implemented by the Pittsburgh Energy Technology Center (PETC). PETC is also responsible for implementation of other related research programs, including coal preparation and direct coal combustion, and has been involved in flue gas cleanup since the late 1950's.

The current DOE program is being conducted by a cross-section of industrial organizations, not-for-profit research laboratories of universities, national laboratories, and in-house research. Many of the projects are new, and the research is just beginning. A chronology and overview of the program, together with brief descriptions of the status of individual projects, are given.

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## DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

## BACKGROUND

### PROGRAM OVERVIEW

The Flue Gas Cleanup Program was initiated in DOE during 1979 as part of the Advanced Environmental Control Technology (AECT) program, and originally included the lime/limestone scrubber program, the advanced flue gas desulfurization (FGD) program, and the $NO_x$/particulate program.

The program supports the development of post-combustion flue gas cleanup technology. The goal of this program is to help foster the more widespread use of coal by providing the technology necessary for its utilization in an environmentally and economically acceptable manner.

The DOE Flue Gas Cleanup Program, like many other Federal research and development (R&D) programs, was reoriented in the 1981-1982 period to emphasize longer-range objectives. Accordingly, those FGD projects aimed at developing improved near-term FGD technologies were curtailed, and attention was shifted toward the needs of the future. Programmatic changes included the following:

- Phaseout of the lime/limestone scrubber projects.
- Phaseout of the advanced FGD projects (dry scrubbing, regenerable processes, etc.).
- Cancellation of the cooperative effort with EPA on the LIMB program.
- Redirection of the $NO_x$/particulate flue gas projects to longer-range combined $NO_x$/$SO_x$/particulate projects.

### PROGRAM RATIONALE

In order to develop the new program rationale and to develop new long-range program objectives, discussions were held within DOE and with EPA, EPRI, TVA, and others.

Coal usage was projected to about double by the year 2000 (Table 1).* With increased coal usage, emissions of $SO_2$, $NO_x$, and particulates could be expected to increase correspondingly unless controlled. Emissions under four possible control scenarios are listed in Table 2. From Table 2, it can be seen that under current NSPS, while $SO_2$ emissions increase only moderately by the year 2000, $NO_x$ emissions about double in the same period. Because of these analyses, the increased international concern with acid precipitation, and the historical pattern followed in Japan, it was concluded that $NO_x$ control will probably receive increased attention during this time period. Interim R&D targets selected were the following:

- $NO_x$ - 70% to 90% control level.
- $SO_2$ - NSPS (90% for high sulfur coal).
- Particulates - NSPS plus further restrictions on respirable particles (<2 microns).

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* "DOE's Electron-Beam Irradiation Developmental Program", by Edward C. Trexler, paper presented at the Seventh Symposium on Flue Gas Desulfurization (May 17-20, 1982).

## TABLE 1. FLUE GAS CLEANUP-PROJECTED* COAL CONSUMPTION (QUADS/YR)

| Sector | 1980 | 1990 | 2000 |
|---|---|---|---|
| o Utility | 11.4 | 17.3 | 23.0 |
| o Industrial | 3.9 | 3.7 | 4.6 |
| o Residential/Commercial | 0.3 | 0.2 | 0.2 |
| o Transportation | - | - | - |
| o Synthetic Fuels | | | 0.4 |
| Total | 15.6 | 21.2 | 28.2 |

* National Energy Policy Plan, 1983

## TABLE 2. FLUE GAS CLEANUP POLLUTANT EMISSIONS VS. CONTROL LEVEL (COAL-FIRED UTILITY)

| Pollutant | Control Level | Generation/Emission ($10^6$ tons per year) 1980 | 1990 | 2000 |
|---|---|---|---|---|
| $NO_x$ | 0 (uncontrolled) | 4.9 | 7.5 | 9.9 |
| | 1 (NSPS) | 4.6 | 6.4 | 8.1 |
| | 2 (NSPS/low $NO_x$)* | - | 4.9 | 5.2 |
| | 3 (retrofit)* | - | 0.9 | 1.2 |
| $SO_2$ | 0 | 23.1 | 35.2 | 46.8 |
| | 1 | 16.0 | 17.8 | 19.5 |
| | 2 | - | 17.8 | 19.5 |
| | 3 | - | 5.2 | 6.9 |
| TSP | 0 | 46.0 | 70.2 | 93.2 |
| | 1 | 1.0 | 1.1 | 1.2 |
| | 2 | - | 1.1 | 1.2 |
| | 3 | - | 0.26 | 0.35 |

* Control Levels:
Level 2 - NSPS with $NO_x$ lowered to 0.1 #/MMBtu
Level 3 - Retrofit all plants to Level 2 by 1990

To further help establish the DOE Flue Gas Cleanup Program, several studies were made to assess the current status of combined $NO_x/SO_x$/particulate technology. These studies identified technological approaches (summarized in Figure 1); identified specific processes and their developmental status (gas-phase processes are summarized in Figure 2, while liquid-phase processes are summarized in Figure 3); and assessed potential problems associated with each type of process along with possible breakthrough keys (summarized in Table 3). Key technical barriers with possible solutions based on this study are summarized in Table 4.

Based on these studies, it was concluded that combined $NO_x/SO_x$/particulate control technology was not a well developed area; existing processes appeared to be very complicated and likely to be quite expensive. It was therefore decided that the DOE Flue Gas Cleanup Program objectives should be focused on development of simple and economical systems to meet emission limits expected for the late 1980's through the 1990's. The approach was to emphasize combined $NO_x$ and $SO_2$ (and preferably also particulates) in a single reactor. Simple, economical processes that minimize the use of premium fuels or their derivatives (i.e., $NH_3$) and that produce either a useful or benign waste product should be sought. Selective catalytic reduction coupled with limestone scrubbing (SCR/FGD) was selected as a yardstick by which to assess the potential of processes selected for evaluation under the DOE Flue Gas Cleanup Program. Processes selected should have a potential savings of at least 20% to 25% compared to SCR/FGD.

## CURRENT PROGRAM DESCRIPTION

Using the guidelines established, the DOE Flue Gas Cleanup Program was developed. The major focus is the evaluation of combined $NO_x/SO_x$/particulate processes showing potential for meeting the criteria established. For discussion purposes, the projects have been broken down into the following categories: Energy Technology Center (ETC) and National Laboratory projects, electron-beam (E-Beam) projects, support studies, recently completed projects, and projects initiated in late-1983. In the following section, specific projects under each of these categories will be discussed in more detail, including their current status.

## PROJECT DESCRIPTIONS AND CURRENT STATUS

### ENERGY TECHNOLOGY CENTER AND NATIONAL LABORATORY PROJECTS

Current Energy Technology Center projects under the Flue Gas Cleanup Program include projects with Pittsburgh Energy Technology Center (PETC), Grand Forks Project Office (GFPO, formerly Grand Forks Energy Technology Center), and Morgantown Energy Technology Center (METC). A brief summary of the ETC and National Laboratory activities is shown in Table 5.

### Pittsburgh Energy Technology Center Projects

PETC has been involved in flue gas cleanup research for more than twenty years. Recent (1981-1983) activity under the DOE Flue Gas Cleanup Program

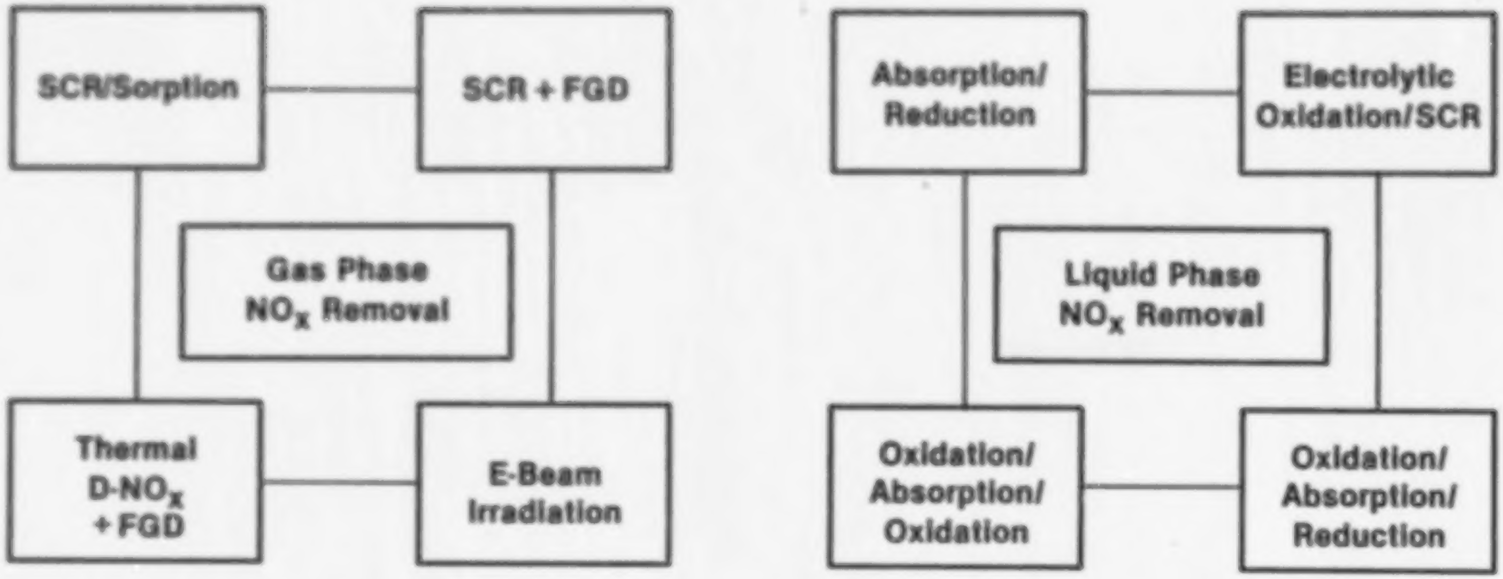
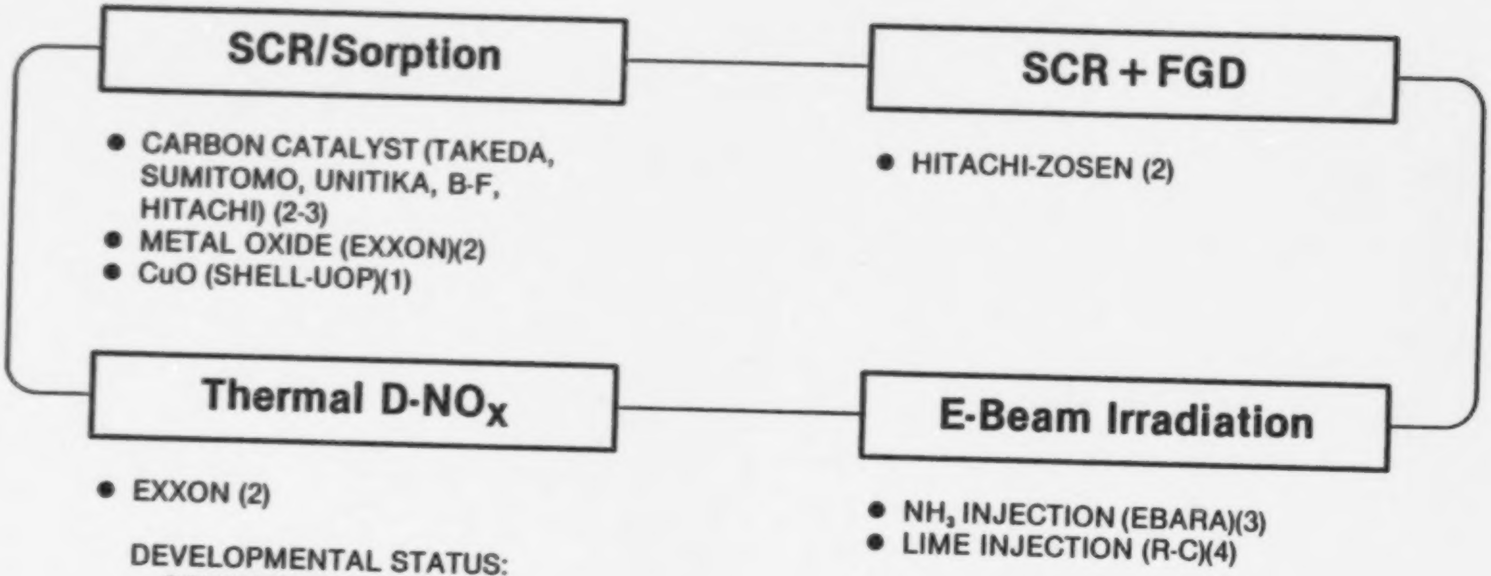

SCR/Sorption
SCR + FGD
Gas Phase NO$_X$ Removal
Thermal D-NO$_X$ + FGD
E-Beam Irradiation
Absorption/ Reduction
Electrolytic Oxidation/SCR
Liquid Phase NO$_X$ Removal
Oxidation/ Absorption/ Oxidation
Oxidation/ Absorption/ Reduction

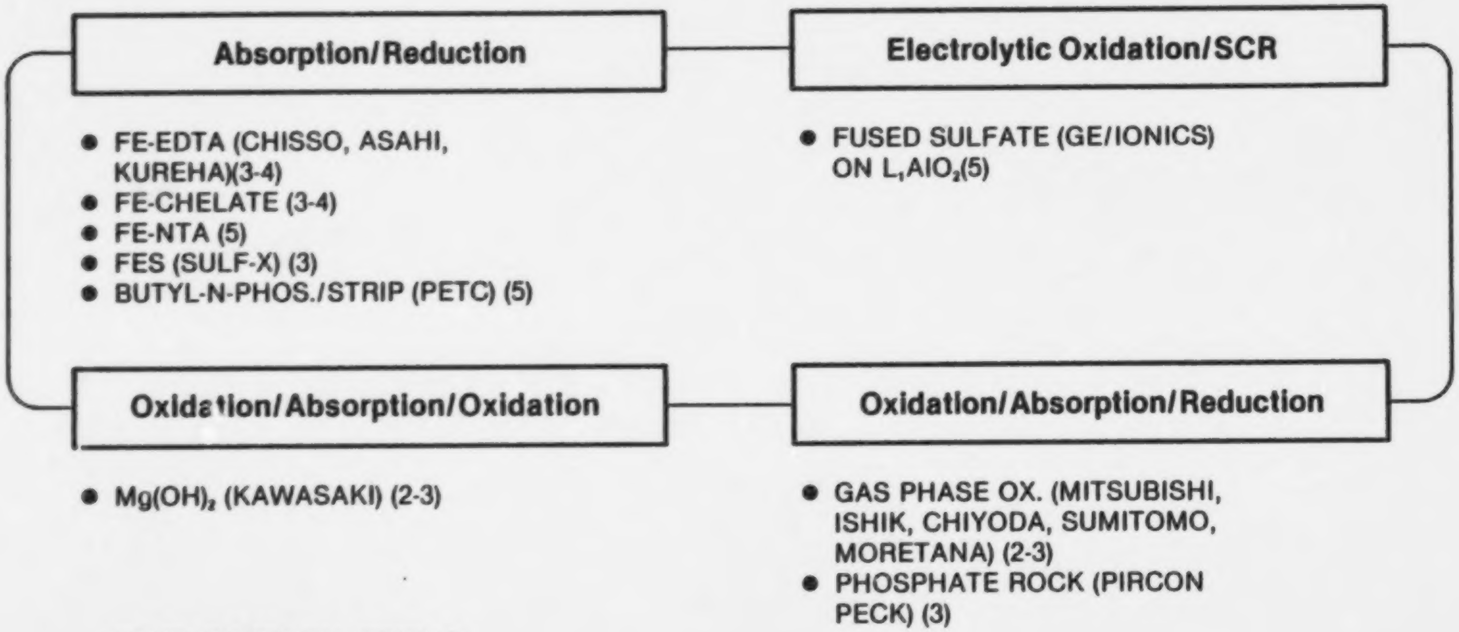
Figure 1. Flue Gas Cleanup NO$_X$/SO$_X$ Removal — Technological Approaches —



DEVELOPMENTAL STATUS:

| | |
|---|---|
| COMMERCIAL | — (1) |
| PILOT | — (2) |
| PDU | — (3) |
| BENCH | — (4) |

Figure 2. Flue Gas Cleanup $NO_x$/$SO_x$ Removal — Gas Phase Technology —



**Absorption/Reduction**

- FE-EDTA (CHISSO, ASAHI, KUREHA)(3-4)
- FE-CHELATE (3-4)
- FE-NTA (5)
- FES (SULF-X) (3)
- BUTYL-N-PHOS./STRIP (PETC) (5)

**Electrolytic Oxidation/SCR**

- FUSED SULFATE (GE/IONICS) ON $L_1AIO_2$(5)

**Oxidation/Absorption/Oxidation**

- $Mg(OH)_2$ (KAWASAKI) (2-3)

**Oxidation/Absorption/Reduction**

- GAS PHASE OX. (MITSUBISHI, ISHIK, CHIYODA, SUMITOMO, MORETANA) (2-3)
- PHOSPHATE ROCK (PIRCON PECK) (3)

DEVELOPMENTAL STATUS:
COMMERCIAL — (1)
PILOT — (2)
PDU — (3)
BENCH — (4)
CONCEPT — (5)

Figure 3. Flue Gas Cleanup $NO_X/SO_X$ Removal — Liquid Phase Technology —

## TABLE 3. FLUE GAS CLEANUP $NO_x/SO_x$ REMOVAL TECHNOLOGY ASSESSMENT

| Technology | Drawbacks to Process | Breakthrough Key |
|---|---|---|
| SCR/Sorption | $NH_3$ Cost Sensitivity* | Alternate Source |
| - Carbon Cat. | Use High Carbon and $NH_3$ | More Reactive Sorbents or Catalysts |
| - Metal Oxide | Need Large Reactor | |
| - CuO | Need H-C for Regeneration | Coal Reduction |
| SCR + FGD | $NH_3$ Cost Sensitivity* | Alternate Source |
| | High $NH_3$ and Catalyst | Improved Catalyst |
| | $NH_3$ Breakthrough | Improved Catalyst |
| Thermal D-$NO_x$ | Need High/Close Temp. Control | None? |
| E-Irradiation | High Cost of E-Guns | Lower E-Gun $ |
| | $NO_3$ Disposition (Lime Slurry) | Low Cost $NO_3$ Disp./Util. |
| | $NH_3$ Cost Sensitivity ($NH_3$ Inj.)* | Alternate Source |
| Absorption/ Reduction | Need High L/G and Large $R_x$ | Higher Reactivity (Catalyst Dev.) |
| | Limited to High Sulfur Coal | |
| Electrolytic-Oxidation/SCR | Unknown | More Data |
| Oxidation/ Absorption/ Reduction | High Cost of Ozone or $ClO_2$ | Low Cost Ozone |
| | Creates Waste $NO_3$ | Low Cost $NO_3$ Disp./Util. |
| | Need Catalyst if Insoluble Absorbent | Improved Catalyst |
| | May Create Waste $Na_2SO_4$ | $Na_2SO_4$ Fixation |
| Oxidation/ Absorption/ Oxidation | Creates Waste $NO_3$ | Low Cost $NO_3$ Disp./Util. |

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* Operating cost of processes that rely on $NH_3$ to reduce $NO_x$ will increase significantly if $NH_3$ cost increases by factor of 3.9 by 1990, as predicted for its natural gas feedstock.

## TABLE 4. FLUE GAS CLEANUP $NO_x$/$SO_x$/PARTICULATE REMOVAL
## KEY TECHNICAL BARRIERS

o $NO_x$

- "NO" is generally insoluble and unreactive.

  Solution:

  A) Find additive for reducing NO to $N_2$.

  B) Find additive to convert NO to a water-soluble species.

o $SO_2$

A) Slurry sorbents (Ca base) require high L/G; scale and create sludge.

B) Solution sorbents (Na base) produce a highly soluble $Na_2SO_4$ waste (arid regions only).

Solution:

A) Dual alkali: solution sorbents are regenerated with Ca.

B) Forced oxidation used to convert sludge to gypsum.

C) Spray dryer produces dry waste materials.

o Particulates

- High resistivity ash (ESP)

  Solution:

  Use precharger or add conditioners.

- High $\Delta P$ (baghouse)

  Solution:

  Use electrostatic bag.

TABLE 5. ETC AND NATIONAL LABORATORY ACTIVITIES

| Organization | Activity |
|---|---|
| PETC | Experimental studies with fluidized-bed CuO absorber and regenerator. |
| GFPO | Calcium compound injection, followed by selective catalytic reduction with high-temperature baghouse. Evaluation of particulate control technology. |
| METC | Measurement of ultrafine particulate matter and mechanisms of aerosol formation. |
| ANL | Enhancement of $NO_x$ removal by aqueous scrubber chemistries. Low-temperature, gas-phase reduction of $NO_x$. |
| LBL | Mechanistic studies of coordination of NO to metal chelates, reaction between nitrosyl metal chelates and absorbed $SO_2$, and NO oxidation by $O_2$ activated on metal chelates. |

included testing of a lime spray dryer on high sulfur Eastern coal in a 500-lb coal/hr test facility; dry injection using nahcolite, trona, and sodium bicarbonate; equilibrium studies of adsorption/steam stripping; and bench-scale tests to evaluate the fluidized-bed copper oxide combined $NO_x/SO_x$ process in a six-inch-diameter fluidized-bed test unit.

The PETC fluidized-bed copper oxide process is chemically identical to the Shell/UOP process, which was tested earlier under a joint DOE/EPA program at Tampa Electric Company's Big Bend Station in North Ruskin, Fla. The processes differ primarily in the contactor. The PETC concept uses a lower cost fluidized bed, while the Shell/UOP process uses a parallel passage fixed-bed reactor.

The PETC tests on the six-inch-diameter fluidized-bed system appeared so promising that the process was scaled up and tested on the 500-lb coal/hr test facility during 1983. Potential advantages and disadvantages of the fluidized-bed design are shown in Figure 4. Testing has been completed and major preliminary test results are summarized in Table 6.

The major problem encountered during the recent tests was sorbent attrition. The sorbent support material is alumina spheres which are impregnated with copper. Attrition losses of about 0.5% were observed during the recent tests, which is over ten times greater than in similar tests in the six-inch bench-scale unit. Such losses are a key variable in determining makeup requirements, which, in turn, strongly impact the economic feasibility of the process. The attrition losses observed are considered excessive. A test program has been developed for FY84 to identify and correct the cause(s) of the attrition problem.

A preliminary cost estimate for the fluidized-bed copper oxide process to produce sulfuric acid was made by Science Management Corporation, using the EPRI-recommended cost guidelines for a 500-MW utility boiler application burning a 3.5% sulfur coal. The results indicate capital investment of $93/kW to $98/kW, and levelized revenue requirements of 12 mills/kW-hr (without credit). Although the cost estimates have been carefully reviewed by DOE, we plan to submit them for independent analysis by TVA or EPRI or both.

## Grand Forks Project Office Projects

The GFPO manages the University of North Dakota Energy Research Center (UNDERC) in research primarily related to low-rank coals, including North Dakota lignites. Prior activity under the DOE Flue Gas Cleanup Program includes lime spray dryer studies and dry scrubbing in a baghouse, using both trona and nahcolite applied to low-rank-coal-fired boilers. Limestone boiler injection studies and characterization of low-rank-coal ashes have also been included.

The GFPO is currently making an assessment of boiler injection of calcium compounds followed by selective catalytic reduction using a high-temperature baghouse. Small-scale tests have been conducted using an alternate material for boiler injection to replace the limestone normally used. The material is pressure-hydrated lime and shows promise for substantially improved $SO_2$

## Advantages

- Absorber and regenerator can operate at different temperatures.
- No valve problems.
- Constant absorber and regenerator offgases.
- No fly ash buildup.

## Disadvantages

- Possible higher pressure drop.
- Attrition potential.

Figure 4. Fluidized-Bed Design (CuO)

TABLE 6. RESULTS OF COPPER OXIDE TESTING IN THE 500-LB/HR COMBUSTION TEST FACILITY

| | Test Number | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| $SO_2$ Removal, % | 90 | 91 | 91 |
| $NO_x$ Removal, % | 93 | 94 | 93 |
| Inlet $SO_2$ (dry), ppm | 2354 | 2680 | 3100 |
| Inlet $NO_x$ (dry), ppm | 520 | 500 | 510 |
| Bed Temperature, °F/°C | 750/400 | 750/400 | 760/404 |
| Mole $SO_2$ Removed per Mole Available Cu | 0.57 | 0.506 | 0.532 |

removal, at lower stoichiometries, compared to limestone. For 1984, they are planning to coordinate larger-scale field tests at the Hoot Lake Station, where limestone boiler injection tests were conducted earlier.

Also in progress at UNDERC are studies to characterize low-rank coal (LRC) particulates. This effort includes measurement of trace metal species found in LRC fly ash.

## Morgantown Energy Technology Center Projects

The METC project consists of a basic research study involving the measurement of ultrafine particulate matter and mechanisms of aerosol formation. The two-year study project will be initiated during 1984.

## Argonne National Laboratory (ANL) Projects

ANL has initiated a research effort in 1983 for the enhancement of $NO_x$ removal by aqueous scrubber chemistries and by low-temperature, gas-phase reduction of $NO_x$. Most of this year has been devoted to literature searches and bench-scale tests of a variety of additives for wet scrubbers to enhance $NO_x$ removal. Work in FY84 will emphasize novel approaches to low-temperature $NO_x$ reduction.

## Lawrence Berkeley Laboratory (LBL) Projects

For the past three years, the LBL effort under the Flue Gas Cleanup Program has been directed toward basic aqueous chemistry studies pertaining to reactions involved in combined $NO_x/SO_x$ processes. The work has primarily centered on the chemistry of aqueous metal chelate systems, similar to those used in several Japanese wet $SO_2/NO_x$ cleanup processes.

Workers at LBL have measured rate and activity coefficients, have developed metal chelates with at least an order of magnitude improved reaction rates compared to NTA and EDTA, and have developed methods to avoid the large catalyst losses and high water usage encountered earlier with these types of processes in Japan.

## ELECTRON-BEAM PROJECTS

The E-Beam projects were among the first initiated under the DOE Flue Gas Cleanup Program. A paper entitled "DOE's Electron-Beam Irradiation Developmental Program" was presented by Edward C. Trexler at the last FGD Symposium in Hollywood, Fla. The specific projects were described in detail at that time, and only a brief description and update of their current status will be given in the following section.

There are two major projects: one with Research-Cottrell to evaluate the E-Beam/lime spray dryer process, and another with Ebara International Corporation to evaluate the E-Beam/ammonia injection process. Other E-Beam projects include a kinetic study by the AVCO Everett Research Laboratory, and a study by Florida State University of an E-Beam precharger to improve fine particulate capture. The various projects are summarized in Table 7.

## TABLE 7. DOE SUPPORTED E-BEAM PROCESSES AND SUPPORT STUDIES

Program Elements

| E-Beam/Ammonia Process | E-Beam/Lime Process | E-Beam Kinetics | E-Beam Overview |
|---|---|---|---|
| 10-20,000 SCFM PDU Slipstream | 10,000 ACFM PDU Slipstream | Bench-Scale Tests and Modeling | Independent Studies |
| Eastern High Sulfur Coal | Eastern High Sulfur Coal | 18 Months | |
| Optimization Test | Optimization Test | | |
| Reliability Tests | Nitrate Fixation Tests | | |
| Fertilizer Studies | E-Gun Cost Reduction Studies | | |
| Ebara | Research-Cottrell | | |
| Cost Share | Cost Share | | |
| 2 Years | 2 Years | | |

E-Beam chemistry is briefly summarized in Figure 5. A more detailed discussion of the E-Beam chemistry and the E-Beam program can be found in the paper by Edward C. Trexler mentioned above. Potential benefits are shown in Figure 6, and comparative costs of E-Beam versus other possible options are given in Table 8. However, caution is advised at this time, since the E-Beam cost data are very preliminary. Costs are presently used as a guide to assess the future potential of the technology -- not as a basis for judgment concerning commercial application. The E-Beam process costs are highly sensitive to the cost of the E-Beam guns, the relative cost of ammonia versus the sale price of fertilizer by-product (for the ammonia injection process), and the cost of by-product disposal (for lime spray dryer process). All of these factors will be studied in detail during the future course of the project effort.

## Spray Dryer/E-Beam Project

This project is being conducted at TVA's Shawnee Steam Plant near Paducah, Ky. Actually, two separate test programs are planned at Shawnee by Research-Cottrell, one for DOE and another for TVA. The overall effort is cooperatively funded by DOE, TVA, and Research-Cottrell. An overall schematic of the process is shown in Figure 7. A dry landfill waste material is produced from this process.

Due primarily to contractual problems, the project is approximately nine months behind schedule. Installation of equipment at Shawnee also could not be started until the contractual arrangements had been resolved.

Construction at Shawnee should be completed in October 1983, after which shakedown tests are scheduled. The DOE test program will be conducted over a six-month period.

## Ammonia Injection/E-Beam Project

This project will be conducted by Ebara International Corporation at Indianapolis Power and Light's E. W. Stout plant. (Originally, AVCO had the lead role and designed the test facility under a previous DOE contract, with Ebara in a support role.) The project will be cost-shared between DOE and the private sector. Private sector funding has now been secured and includes Ebara, the State of Indiana, several Indiana-based utilities, a coal company, and a fertilizer company.

Contractual arrangements were completed in late September 1983, and construction of the test facility has now been initiated. An overall schematic of the process is shown in Figure 8. The test program will be conducted over a twelve-month period. A dry fertilizer by-product is produced from this process.

## E-Beam Kinetic Study

A study of E-Beam kinetics to develop a model of the process was initiated in 1982. This effort is scheduled for completion in December 1983. A final report will be issued and the model developed will be made available for use.

1. Flue gas is cooled and moisture added.

2. Electron beam bombards flue gas components to produce neutral dissociated atoms.

3. Dissociated atoms react with $NO_x$ and $SO_x$; reactions produce $NO_x$ and $SO_x$ acids.

4. $NO_x$ and $SO_x$ acids react with $NH_3$ (in Ebara process) and CaO (in Research-Cottrell process) to form solid ammonium or calcium salts, respectively.

Figure 5. E-Beam Chemistry

- Preliminary estimates show potential savings of 20% to 25% compared to lime/limestone scrubber coupled with selective catalytic reduction (SCR).

- Dry system, which produces a dry product.

- Fertilizer product may be salable (for Ebara process).

- Dry product may be disposed of easily (for Research-Cottrell process).

Figure 6. E-Beam Potential Benefits

TABLE 8. COMPARATIVE COSTS: E-BEAM VS. OTHER OPTIONS

| $SO_x$ and $NO_x$ Control Approach | Capital Cost ($/kW) | Operating Cost (mills/kW-hr) |
|---|---|---|
| Lime/Limestone Scrubber Plus Separate $NO_x$ Control | 255 | 22 |
| Lime Spray Dryer Plus Separate $NO_x$ Control | 220 | 19 |
| Mature E-Beam Combined $NO_x/SO_x$ System | 205 | 15 |

Reference Footnote on page 2.

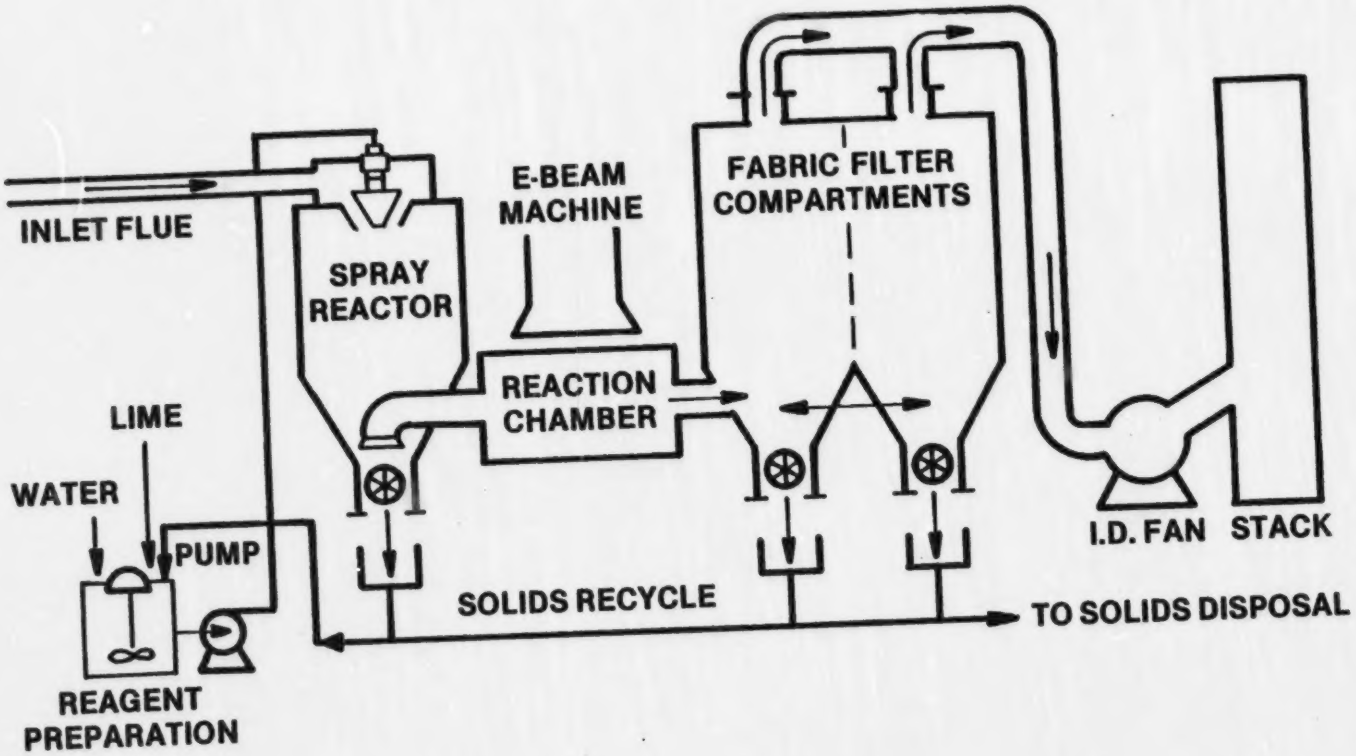

Figure 7. The Spray Dryer, Electron-Beam System

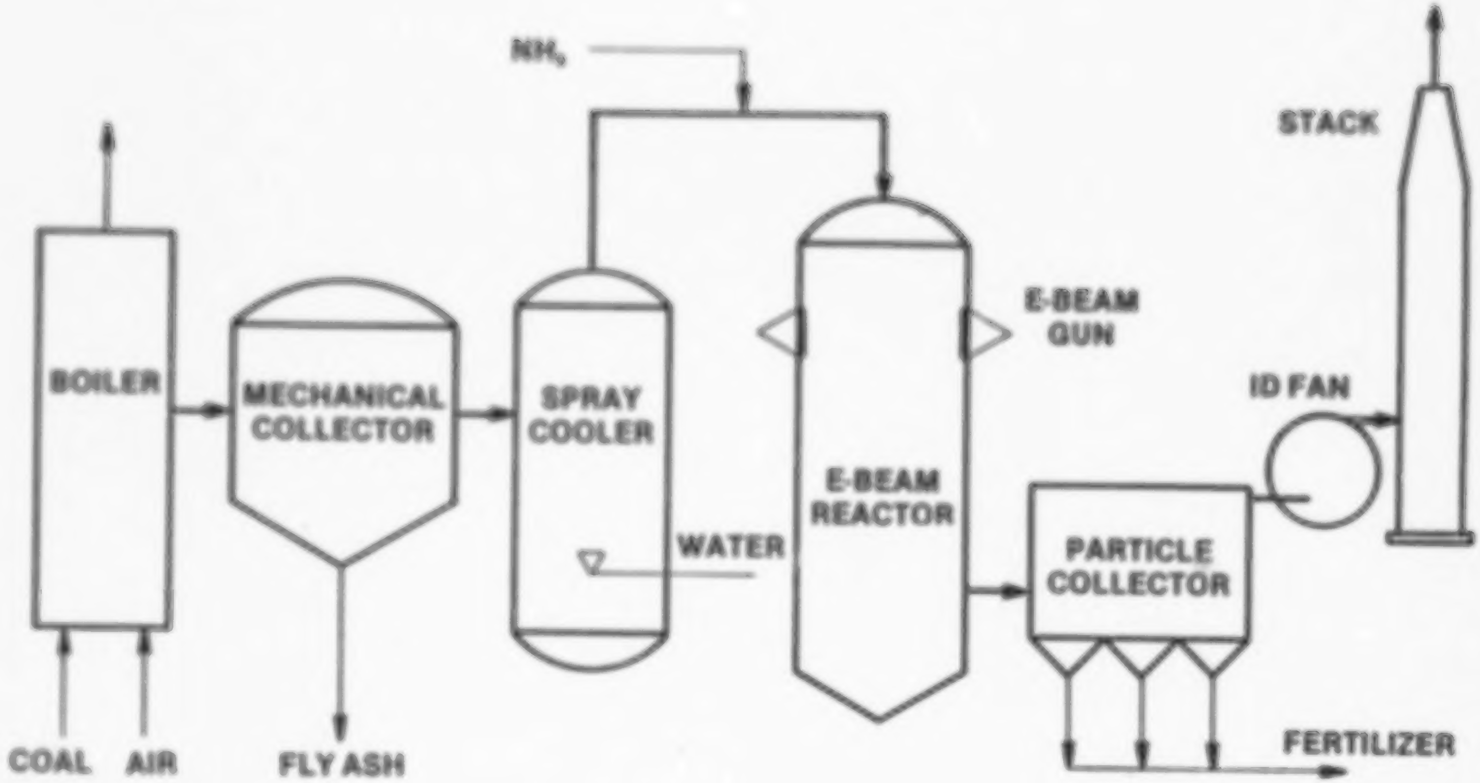

Figure 8. Ebara E-Beam Process Schematic Diagram

## E-Beam Precharging Study

This study is being conducted at Florida State University (FSU) under a DOE contract initiated in late 1980. The precharger shows promise for substantial improvement in fine particulate capture. Numerous mechanical problems have been encountered in setting up the test apparatus, which is shown schematically in Figure 9. Testing has been initiated and will continue during the next two years.

## SUPPORT STUDIES

### Acoustic Agglomeration Study

This project was initiated with the Pennsylvania State University in 1980 to evaluate acoustic agglomeration as a means to improve capture of fine particulates. The original work using various aerosol materials has been completed and a final report is being published.

The results appear promising, but additional work was recommended to improve performance and to run tests on an actual flue gas from an operating coal-fired boiler. These additional data are needed to verify and improve the model. A follow-on contract has been negotiated and further work is now in progress.

### Chemical Thermodynamic Studies

This project was initiated with the National Bureau of Standards (NBS) in 1980 under the lime/limestone scrubber program. Under an Interagency Agreement, NBS was to study the basic chemical thermodynamics and kinetics of $SO_2$ reactions involved in FGD processes for the purpose of establishing a data base for these reactions. As part of the redirection of the Flue Gas Cleanup Program to combined $NO_x/SO_x$ removal, the effort was redirected to emphasize the chemical thermodynamics of reactions involved in combined $NO_x/SO_x$ processes, and to establish a data base for these reactions.

### Systems Study of Integrated Environmental Control Technologies

This project is being conducted by Carnegie-Mellon University, Pittsburgh, Pa. The effort will primarily involve the expansion of existing computer-based models capable of analyzing power plant control options for conventional air pollution control technologies from pre-combustion through post-combustion. Previous studies in this area have been sponsored by both EPA and DOE. The current effort will be to integrate results from the advanced combined $NO_x/SO_x$/particulate projects, as they become available, into the overall system capability. This should provide even greater flexibility in assessing overall control options to optimize multimedia environmental emissions, energy efficiency, resource requirements, and economic costs. The model may also be useful in helping to guide future research efforts. The project is just now getting underway.

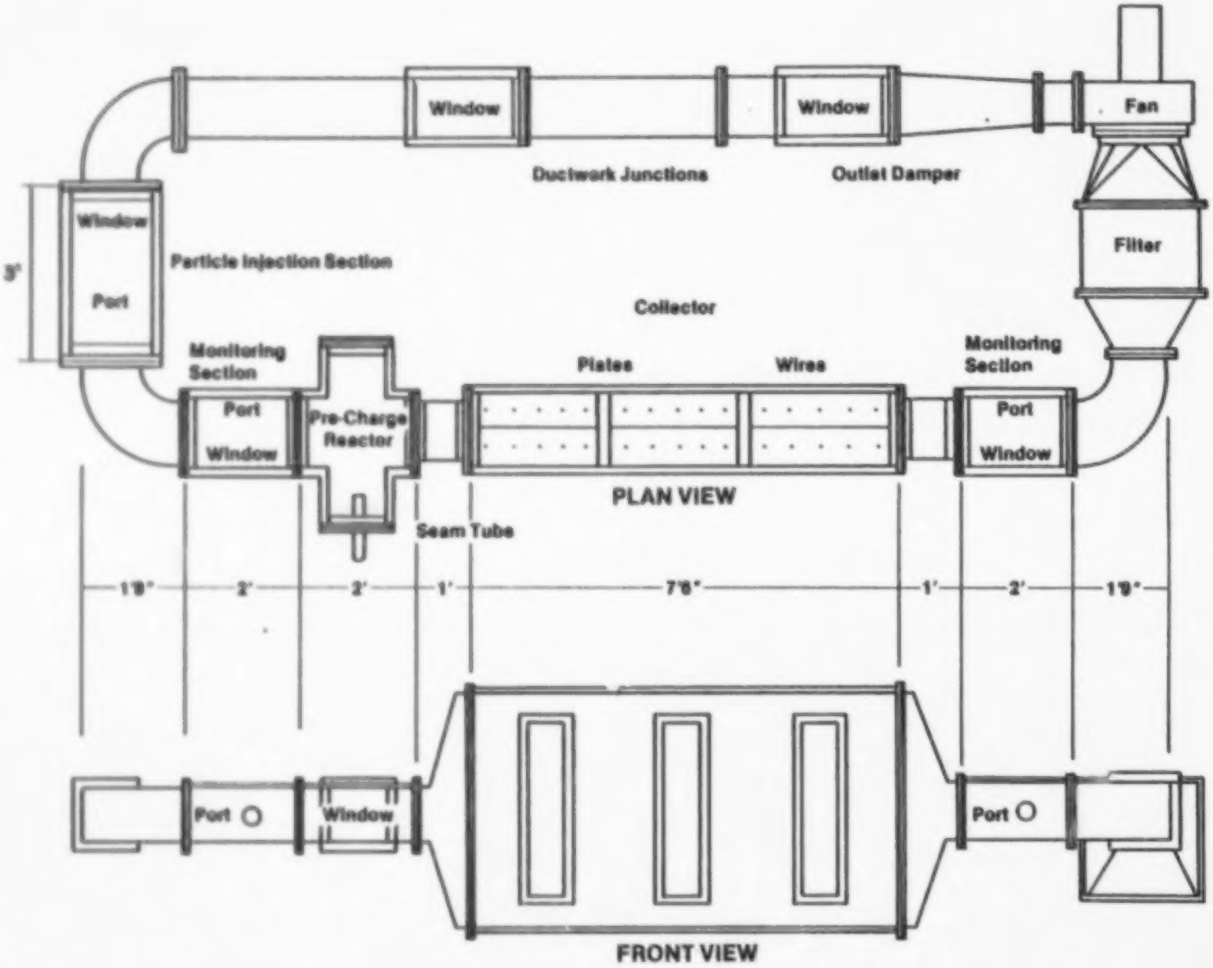

Figure 9. FSU Electron-Beam Precipitator Test System

## PROJECTS NEARING COMPLETION

### Spray Dryer/Limestone Injection Pilot Evaluation

This project was conducted for DOE by Babcock and Wilcox (B&W) at their Alliance, Ohio, Research Center using high sulfur Eastern coal. The project has been completed and the final report is being prepared. A separate paper discussing the results will be presented by John Doyle, of B&W, at this Symposium.

### NOXSO Process Pilot Evaluation

Briefly, the NOXSO process utilizes a dry sodium/alumina sorbent operating in a fluidized-bed adsorber at about 120°C to obtain 90% removal of both $SO_2$ and $NO_x$. The catalyst is regenerated by reaction with $H_2S$ at about 550°C, to produce elemental sulfur. The $NO_x$ is converted to $N_2$ during regeneration. A simplified process schematic is shown in Figure 10.

The present NOXSO catalyst is, in some ways, similar to alkalized alumina, which was tested extensively by the U. S. Bureau of Mines at Pittsburgh (predecessor to PETC). The primary problem with the original alkalized alumina process was excessive sorbent attrition loss. The NOXSO sorbent is prepared by impregnation of sodium on a very attrition-resistant support supplied by the Davison Corp., while the original alkalized alumina was prepared by co-precipitation. Additionally, the NOXSO absorption step operates at about 120°C, while the alkalized alumina absorption was done at about 325°C. Attrition was found to be a strong function of temperature as well as other variables.

During the current bench-scale test program, which extends through December 1983, a number of sorbents were tested for 5-20 cycles to identify the impact of process conditions and sorbent composition on attrition, $SO_2$ and $NO_x$ removal, and capacity. It appears from these tests that attrition can be kept at acceptably low levels. $SO_2$ and $NO_x$ removals are over 90%.

## PROJECTS INITIATED IN LATE-1983

To solicit ideas for the newly reoriented program, a Program Research and Development Announcement (PRDA) for Advanced Combined $NO_x/SO_x$/Particulate Control Processes was issued in 1982. The solicitation resulted in fourteen responses, which were evaluated and rated according to predetermined evaluation criteria specified in the PRDA. Five of the most promising proposals were selected early in 1983 for negotiation for contract award. For the most part, these contracts have only recently been signed, and work is just beginning. The five projects are described below.

### Glow Discharge Irradiation Process Evaluation

The project is being conducted by Westinghouse R&D Center, Pittsburgh, Pa. The process is based on the concept of glow discharge irradiation of the flue gas stream to remove high levels of both the $NO_x$ and $SO_2$ without ammonia addition. In concept, the process is similar to the E-Beam irradiation

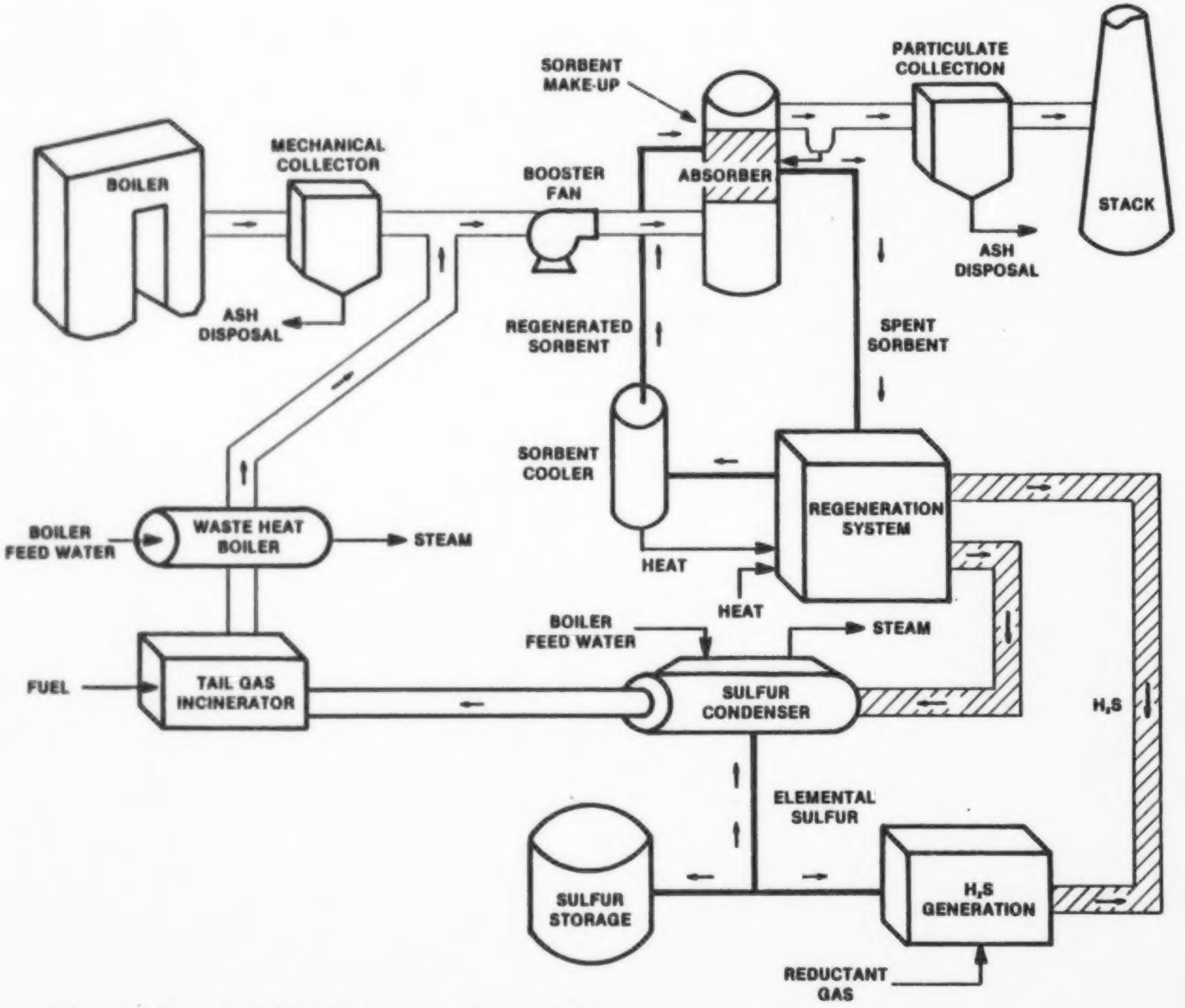

Figure 10. NOXSO Process Flow Diagram

processes. Potential advantages include the following: (1) less power is required than for the E-Beam; (2) no additives, such as ammonia, were proposed; however, one of the key questions is whether the by-product material will be salable as a fertilizer without additives; and (3) the process is potentially a simple, low-cost system that should require no radiation protection and that could even be installed in the existing ductwork.

A separate downstream particulate collection device would be required. Small bench-scale tests are first planned to study the concept further. If these are promising, a small pilot plant will be constructed and operated on an actual coal-fired boiler flue gas for evaluation. The project is just now getting underway, and if the process works as proposed, it could be a very attractive, simple, low-cost system applicable to either new or retrofit situations.

## Moving-Bed Copper Oxide Process Evaluation

The project is being conducted by Rockwell International, Canoga Park, Calif. The process chemistry is similar to those of the Shell/UOP fixed-bed and the PETC fluidized-bed copper oxide processes. Since the proposed process involves continuous sorbent circulation through a moving-bed filter, it should retain all of the potential advantages of PETC's fluidized-bed approach, with the added advantage of obtaining $NO_x$, $SO_2$, and particulate control in a single reactor vessel.

Copper oxide processes have been tested adequately to demonstrate that they work well for up to 90% control of $SO_2$ and $NO_x$. Therefore, the thrust of this project will be to evaluate the capability of the proposed process to also control particulate simultaneously with $SO_2$ and $NO_x$ in a cost-effective manner. This implies meeting the targeted control levels for $SO_2$, $NO_x$, and particulates at a reasonable pressure drop and without excessive catalyst attrition losses. The approach will be to modify and test an existing relatively small-scale contactor/filter on a simulated coal-fired flue gas for further evaluation. If these tests appear promising, the process may be scaled up to a larger pilot plant size for testing on actual coal-fired flue gas. The project is just now getting underway and is the only process being tested with the potential to control all three -- $SO_2$, $NO_x$, and particulates -- in a single reactor vessel.

## Sulf-X (FeS-Based System) Process Evaluation

The project is being conducted by NUS Corporation, Gaithersburg, Md. The process concept is not new. A test facility has been installed and operated at the Western Center Hospital in Canonsburg, Pa., for the past two years. The process is based on aqueous absorption of $SO_2$ and $NO_x$, using a slurry of FeS that can be prepared from waste products. The spent reagent is regenerated with coal or coke to produce sulfur. Results to date indicate that up to 90% $SO_2$ control and over 40% $NO_x$ removal can be achieved with the present unit. Modifications of the absorber were proposed to increase $NO_x$ absorption to 90%.

## Zinc Oxide Spray Dryer Process Bench-Scale Tests

The project is being conducted by Battelle Columbus Laboratory. The process concept is based on the use of ZnO in a spray dryer to remove up to 90% of both $SO_2$ and $NO_x$. Only limited fixed-bed data were available, especially for $NO_x$ control. Small bench-scale tests are planned at this time to further evaluate whether or not the proposed concept shows potential for further testing. The project is just now getting underway.

## Zeolite Catalyst (Using Fe or Cu) Process Bench-Scale Tests

The project is being conducted by Science Applications, Inc., San Diego, Calif. The process concept is based on the use of a synthetic zeolite catalyst impregnated with Fe or Cu, ammonia addition for $NO_x$ control, and catalyst regeneration to produce either sulfuric acid or elemental sulfur. Only limited work has been done to identify possible candidates for an improved catalyst material. Small bench-scale tests are planned at this time to evaluate the proposed catalysts and determine if they show potential for further testing. The project is just now getting underway.

# SUMMARY

## CURRENT PROGRAM

The current program supports the development of cleanup technology to promote the use of abundant coal resources in an economical and environmentally acceptable manner. Simple, economical processes capable of 90% control of $NO_x$ and $SO_2$, or showing improved capture of fine particulate, preferably in a single reactor vessel, are emphasized. Projects include both DOE and National Laboratory research and contracted efforts with industry, not-for-profit research organizations, and universities. An effort is being made to keep a balanced program between basic research studies, longer-range concepts and ideas, and processes that are at the proof-of-concept stage. Much of the current effort is really just now getting started.

# STATUS OF $SO_2$ AND $NO_x$ REMOVAL IN JAPAN

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Flue gas desulfurization (FGD) capacity in Japan has increased rapidly from 1970, reaching $10^8$ $Nm^3/h$ (33,000 MW equivalent) in 1976, and increasing slowly since. For nitrogen oxide ($NO_x$) removal, selective catalytic reduction (SCR) of $NO_x$ has been used in addition to combustion modification. The SCR capacity increased from $10^6$ $Nm^3/h$ in 1976 to $7 \times 10^7$ $Nm^3/h$ in 1982. A combined flue gas cleaning system (including SCR, electrostatic precipitator (ESP), and FGD) has been applied to industrial boilers and furnaces since 1975 and to coal-fired boilers since 1980 to remove 50-90% of $NO_x$ and 90-95% of $SO_2$. The combined cleaning for coal costs 2-3 yen*/kWh including 7 years depreciation.

Many new coal-fired boilers with the combined cleaning system have been planned because of their economic advantage over the use of low- or high-sulfur oil with FGD, although the recent decrease in oil price has reduced considerably the economic advantage. Efforts have been made to improve the combined system mainly by (1) reducing FGD cost by simplifying or modifying the process and by saving energy, (2) reducing particulate emissions below 30 $mg/Nm^3$ by ESP and wet FGD, and (3) improving gas reheating after wet FGD.

Simultaneous $SO_2$ and $NO_x$ removal processes were studied eagerly between 1973 and 1978 and applied to several small industrial boilers and furnaces but have not been used at a large scale because of the problems involved.

## 1. General Aspects of FGD

Table 1 lists major constructors of FGD plants and numbers and capacities of plants larger than 10,000 $Nm^3/h$ that either are operational or will be complete by the end of 1983. The plants total 470, and their combined capacity reaches 111,000,000 $Nm^3/h$ (equivalent to 36,000 MW). About 60% of the capacity is accounted for by utility boilers, including 6,200 MW for coal-fired boilers. About 50% of all the plants, in terms of capacity, use the wet lime/limestone process to by-produce gypsum; 18% use the indirect lime/limestone process (double alkali type) and modified lime/limestone process; 10% use the regenerable process, by-producing sulfuric acid, ammonium sulfate, and sulfur; and 22% use sodium scrubbing to by-produce sodium sulfite or sulfate. About 80% of the sodium scrubbing plants by-produce sodium sulfite for paper mills. In addition to the 262 sodium scrubbing plants listed in Table 1, there are nearly 900 smaller ones by-producing mainly waste sodium sulfite or sulfate liquor.

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*August 5, 1983 exchange rate: 244 yen = $1

TABLE 1. NUMBERS AND CAPACITIES (1,000 $Nm^3/h$) OF FGD PLANTS IN JAPAN BY MAJOR CONSTRUCTORS (CAPACITY LARGER THAN 10,000 $Nm^3/h$, OPERATIONAL OR TO BE COMPLETED BY END OF 1983)

| Plant constructor | By-product | | | | Total |
|---|---|---|---|---|---|
| | Gypsum | | $H_2SO_4$, S<br>$(NH_4)_2SO_4$ | $Na_2SO_3$<br>$Na_2SO_4$ | |
| | Direct[a] | Indirect[b] | | | |
| Mitsubishi Heavy Industries (MHI) | 41 (25,019) | - | - | 3 ( 292) | 44 ( 25,311) |
| Ishikawajima-Harima H.I. (IHI) | 20 ( 8,633) | - | - | 26 ( 3,240) | 46 ( 11,873) |
| Hitachi Ltd. & Babcock-Hitachi (BHK) | 17 (10,200) | - | 2 ( 590) | 19 ( 843) | 38 ( 11,633) |
| Kawasaki Heavy Industries (KHI) | 2 ( 174) | 11 ( 7,966) | - | 7 ( 256) | 20 ( 8,396) |
| Mitsubishi Kakoki (MKK) | 5 ( 506) | - | 13 ( 6,606) | 3 ( 530) | 21 ( 7,642) |
| Oji Koei (Oji Engineering) | - | - | - | 32 ( 6,239) | 32 ( 6,239) |
| Fujikasui Engineering | 7 ( 4,144) | - | - | 18 ( 1,716)[c] | 25 ( 5,860) |
| Chiyoda Chem. Eng. Construction | 2 ( 470) | 13 ( 4,375) | - | - | 15 ( 4,845) |
| Kurabo Engineering | - | 5 ( 588) | 1 ( 18) | 102 ( 3,912)[c] | 108 ( 4,518) |
| Mitsui Miike Machinery Co. (MMMC) | 6 ( 3,653)[d] | - | 1 ( 520) | - | 7 ( 4,173) |
| Tsukishima Kikai Co. (TSK) | 1 ( 80) | 4 ( 430) | 1 ( 110) | 31 ( 3,553) | 37 ( 4,173) |
| Ebara Corp. (Ebara Manufacturing) | 1 ( 26) | 11 ( 1,520) | - | 10 ( 2,006) | 22 ( 3,552) |
| Nippon Kokan (NKK) | 3 ( 197) | 1 ( 150) | 2 ( 1,990) | - | 6 ( 2,337) |
| Nippon Steel | 2 ( 2,100)[e] | - | - | - | 2 ( 2,100) |
| Kobe Steel | - | 6 ( 1,925) | - | - | 6 ( 1,925) |
| Kureha Chemical Industries (KCI) | - | 1 ( 40) | - | 7 ( 1,380) | 8 ( 1,420) |
| Showa Engineering & Showa Denko | - | 3 ( 1,002) | - | 2 ( 370) | 5 ( 1,372) |
| Mitsui Metal Engineering | 4 ( 1,006) | - | 2 ( 130) | - | 6 ( 1,136) |
| Dowa Koei (Dowa Engineering) | - | 11 ( 1,113) | - | - | 11 ( 1,113) |
| Sumitomo Chemical Engineering (SCEC) | - | - | 5 ( 748) | - | 5 ( 748) |
| Niigata Iron Works | 2 ( 265) | - | - | 2 ( 220) | 4 ( 485) |
| J.G.C. Corp. | 1 ( 330) | - | 1 ( 125) | - | 2 ( 455) |
| Total | 114 (56,803) | 66 (19,109) | 28 (10,837) | 262 (24,557) | 470 (111,306) |

[a] Wet lime/limestone process

[b] Indirect and modified lime/limestone process

[c] Including waste $MgSO_4$ liquor

[d] Including one plant by-producing throwaway sludge

[e] Using convertor slag as the absorbent

Most of the FGD plants were constructed between 1972 and 1977. The growth of the FGD capacity has been slow since 1977 because the ambient $SO_2$ concentrations have been lowered and not many new $SO_2$ sources have been constructed due to the economic depression. The FGD plants constructed since 1978 include 18 plants involving the wet lime/limestone process with a total capacity of 14,600,000 $Nm^3/h$ (4,800 MW, mainly limestone process for coal-fired boilers) and 19 plants involving the indirect and modified lime/limestone gypsum process with a total capacity of 5,700,000 $Nm^3/h$ (1,900 MW). Virtually no plants involving other processes have been constructed since 1978.

Gypsum supply in Japan has been short since 1978 due to the increase in demand and the decrease of by-product gypsum from wet-process phosphoric acid production. Although gypsum by-producing by FGD costs 1.5-2 yen/kWh (6-8 mills/kWh) including 7 years depreciation, the process has been more useful than other processes. FGD processes by-producing elemental sulfur have been used at oil refineries by introducing the recovered $SO_2$ into existing Claus furnaces. A demonstration plant is under construction at a coal-fired power station to by-produce elemental sulfur by the activated carbon process.

## 2. FGD Plants for Coal-Fired Boilers

Table 2 lists coal-fired boilers and their FGD and SCR units. FGD has been applied to nearly all coal-fired boilers except several small ones in Hokkaido (Northern Island) not shown in the Table. All coal-fired boilers have an ESP upstream of FGD to reduce particulates to 50-1,000 $mg/Nm^3$ (removal efficiency 95-99.8%). All FGD units for coal-fired boilers use a wet lime/limestone process (there are six types, shown in Figure 1 and Tables 2 and 3). Type I by-produces throwaway sludge; others by-produce gypsum.

Most of the new FGD plants use Type IV which has a prescrubber with a separate liquor loop. The prescrubber has the following functions: (1) remove fluorine in flue gas which tends to lower $SO_2$ removal efficiency, in combination with other impurities (Figure 2); (2) remove chlorine in flue gas which tends to promote corrosion and lower the $SO_2$ removal efficiency; (3) remove fly ash and increase the purity of by-product gypsum; and (4) cool the gas to prevent scaling and to protect linings in the scrubber. On the other hand, the prescrubber raises the FGD plant cost by 3-7% and increases the wastewater; therefore, it may be eliminated for coals with less impurities that depress the $SO_2$ removal efficiency or when the adverse effect of the impurities is depressed by certain additives.

Most of the new plants use a small amount of sulfur acid to reduce the pH of the calcium sulfite slurry to 4.0-4.5 to attain complete oxidation to by-produce good-quality salable gypsum; however, the units using the Chiyoda jet bubbling reactor (JBR) process (Type V) and the Kawasaki magnesium gypsum process (Type IV), can attain perfect oxidation without sulfuric acid addition.

TABLE 2. FGD AND SCR UNITS FOR COAL-FIRED BOILERS (LARGER THAN 75 MW)

| | | Boiler | | | FGD | | | SCR | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Owner | Plant site | No. | MW | N/R[a] | Constructor | Completion | Type[b] | Constructor | Completion | Type |
| Mitsui Aluminum | Omuta | 1 | 156 | R | MMMC[c] | 1972 | I | | | |
| Mitsui Aluminum | Omuta | 2 | 175 | N | MMMC | 1975 | II | | | |
| EPDC | Takasago | 1 | 250 | R | MMMC | 1975 | II | | | |
| EPDC | Takasago | 2 | 250 | R | MMMC | 1976 | II | | | |
| EPDC | Isogo | 1 | 265 | R | IHI[d] | 1976 | III | | | |
| EPDC | Isogo | 2 | 265 | R | IHI | 1976 | III | | | |
| EPDC | Takehara | 1 | 250 | R | BHK[e] | 1977 | III | BHK, KHI[f] | 1980 | L[l] |
| EPDC | Takehara | 3 | 700 | N | IHI | 1983 | III | BHK | 1983 | L |
| EPDC | Matsushima | 1 | 500[g] | N | IHI, MMMC | 1981 | IV | | | |
| EPDC | Matsushima | 2 | 500[g] | N | BHK, MMMC | 1981 | IV | | | |
| Chugoku Electric | Shimonoseki | 1 | 175 | R | MHI[h] | 1979 | IV | MHI | 1980 | H[m] |
| Chugoku Electric | Shin-Ube | 1 | 75 | R | MHI | 1982 | IV | MHI | 1982 | H |
| Chugoku Electric | Shin-Ube | 2 | 75 | R | MHI | 1982 | IV | MHI | 1982 | H |
| Chugoku Electric | Shin-Ube | 3 | 156 | R | MHI | 1982 | IV | MHI | 1982 | H |

TABLE 2. FGD AND SCR UNITS FOR COAL-FIRED BOILERS (LARGER THAN 75 MW) (Continued)

| | | Boiler | | | FGD | | | SCR | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Owner | Plant site | No. | MW | N/R[a] | Constructor | Completion | Type[b] | Constructor | Completion | Type |
| Chugoku Electric | Mizushima | 1 | 125 | R | BHK | 1984 | IV | BHK | 1984 | H |
| Chugoku Electric | Mizushima | 2 | 156 | R | BHK | 1984 | IV | BHK | 1984 | H |
| Hokkaido Electric | Tomato-Atsuma | 1 | 350[i] | N | BHK | 1980 | IV | BHK | 1980 | L |
| Hokkaido Electric | Tomato-Atsuma | 2 | 600 | N | MHI | 1984 | IV | | | |
| Joban Joint | Nakoso | 8 | 600[j] | N | MHI | 1983 | IV | MHI | 1983 | H |
| Joban Joint | Nakoso | 9 | 600[j] | N | MHI | 1983 | IV | IHI | 1983 | H |
| Kyushu Electric | Omura | 2 | 156 | R | MHI | 1982 | IV | | | |
| Kyushu Electric | Minato | 1 | 156 | R | MMMC | 1983 | III | MHI | 1983 | H |
| Sakata Joint | Sakata | 1 | 350 | N | MHI | 1984 | IV | MHI | 1984 | H |
| Sakata Joint | Sakata | 2 | 350 | N | MHI | 1985 | IV | MHI | 1984 | H |
| Shikoku Electric | Saijo | 1 | 175 | R | KHI | 1983 | VI | MHI | 1983 | H |
| Shikoku Electric | Saijo | 2 | 250 | R | KHI | 1984 | VI | IHI | 1984 | H |

TABLE 2. FGD AND SCR UNITS FOR COAL-FIRED BOILERS (LARGER THAN 75 MW) (Continued)

| Owner | Plant site | Boiler |  |  | FGD |  |  | SCR |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  | No. | MW | N/R[a] | Constructor | Completion | Type[b] | Constructor | Completion | Type |
| Tohoku Electric | Sendai | 2 | 175 | R | BHK | 1983 | IV | BHK | 1983 | H |
| Tohoku Electric | Sendai | 3 | 175 | R | BHK | 1983 | IV | BHK | 1983 | H |
| Tokyo Electric | Yokosuka | 1 | 265[k] | R | MHI | 1985 | IV | MHI | 1984 | H |
| Tokyo Electric | Yokosuka | 2 | 265[k] | R | BHK | 1985 | IV | BHK | 1985 | H |
| Toyama Joint | Toyama | 1 | 200 | R | Chiyoda | 1984 | V | BHK | 1984 | H |
| Toyama Joint | Toyama | 2 | 200 | R | Chiyoda | 1984 | V | BHK | 1984 | H |

[a] New or retrofit

[b] See Figure 1 for type

[c] Mitui Miike Machinery Company

[d] Ishikawajima-Harima Heavy Industries

[e] Babcock-Hitachi K.K.

[f] Kawasaki Heavy Industries

[g] Subjecting 75% of the gas to FGD

[h] Mitsubishi Heavy Industries

[i] Subjecting 50% of the gas to FGD and 25% of the gas to SCR

[j] Burns both coal and oil

[k] Burns coal/oil mixture

[l] Low-dust system

[m] High-dust system

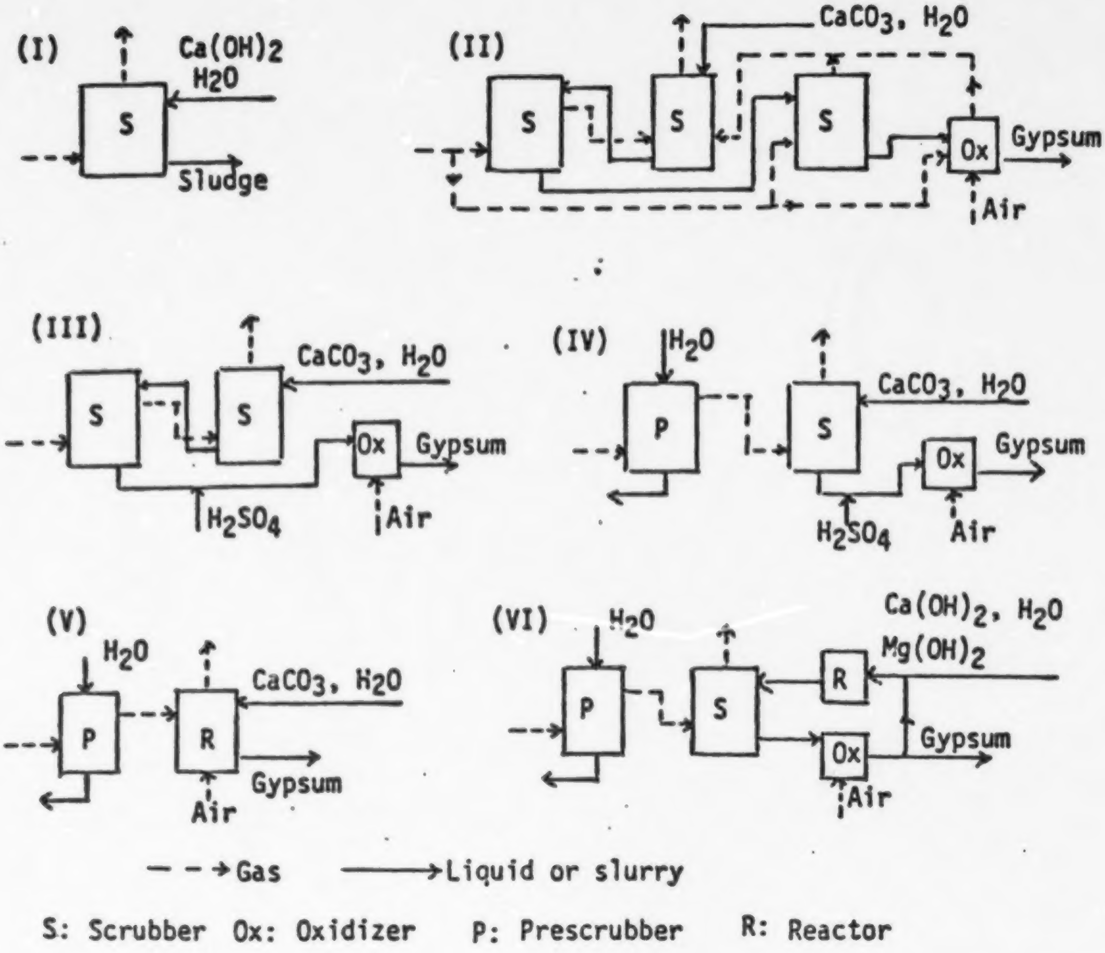


Figure 1. Types of wet lime/limestone process.

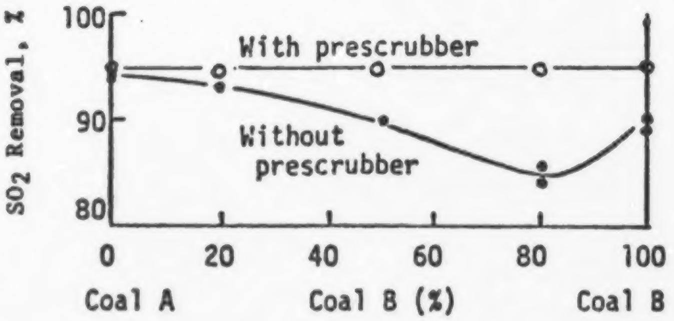


Figure 2. Coal blending and $SO_2$ removal efficiency of the limestone-gypsum process (by Babcock-Hitachi).

TABLE 3. CLASSIFICATION OF WET LIME/LIMESTONE PROCESSES

| Type | By-Product | Absorbent | Additive | Prescrubber[a] | Sulfuric Acid[b] |
|---|---|---|---|---|---|
| I | Sludge | $Ca(OH)_2$ | None | None | None |
| II | Gypsum | $CaCO_3$ | Catalyst | None | None |
| III | Gypsum | $CaCO_3$ | Occasional | None | Yes |
| IV | Gypsum | $CaCO_3$ | None | Yes | Yes |
| V | Gypsum | $CaCO_3$ | None | Yes | None |
| VI | Gypsum | $Ca(OH)_2$ | MgO | Yes | None |

[a] With a separate liquor loop

[b] To lower pH of calcium sulfite slurry to promote oxidation

Two large FGD plants for new coal-fired boilers have started operation in 1983: one is the Takehara plant of EPDC with a 700 MW boiler using a Type III scrubber system in one train; and the other is the Nakoso plant of Joban Joint Power Co. with a 600 MW boiler using a Type IV scrubber system in two trains. Both have been operated without trouble, except a minor start-up problem with a fan at Nakoso, which has been solved. Operating parameters of those plants are shown in Table 4 in comparison with those of two new FGD plants for industrial oil-fired boilers.

The plants in Table 4 are characterized by low power consumption--1.3-2.1% as compared with 1.7-2.6% for conventional plants by-producing gypsum. At the Nakoso and Sendai plants, power consumption decreases at reduced boiler load, while at many conventional plants the power consumption (%) tends to increase at reduced load. The Nakoso and Sendai plants use improved fans that consume less energy at reduced load. Thus the power consumption (%) can be reduced due to the decrease of the pressure drop in addition to the decrease in the gas volume and the slurry recirculation rate. The FGD cost for those plants may be about 1.3 yen/kWh including 7 years depreciation.

Efforts have been made for further improvement of FGD systems for coal. Concerning gas reheating, the Ljungstrom gas-gas heater has been improved to give little gas leakage. Non-leaking gas reheaters have been tested.(1,2) For particulate reduction, wet ESPs (downstream of wet FGD) have been tested.(2)

## 3. FGD Plants for Industrial Boilers Utilizing New Processes

The Yokkaichi plant of Mitsui Petrochemical is the first commercial plant utilizing the Chiyoda 121 JBR process (Table 4). It has the capacity to treat 250,000 $Nm^3/h$ of flue gas from an oil-fired boiler and

### TABLE 4. OPERATING PARAMETERS OF NEW FGD PLANTS (ABSORBENT: LIMESTONE. BY-PRODUCT: GYPSUM. NUMBERS IN PARENTHESES ARE FOR REDUCED LOAD.)

| Owner | EPDC | Joban Joint | Mitsubishi Petrochem. | Toyo Rubber |
|---|---|---|---|---|
| Site, Boiler No. | Takehara, 3 | Nakoso, 8 | Yokkaichi | Sendai |
| Fuel | Coal | Oil, Coal[a] | Oil | Oil |
| Boiler capacity, MW | 700 | 600 | 85 | 14 |
| Gas treated, 1000 $Nm^3$/h | 2200 | 1980 (990) | 250 | 40 (30) |
| FGD constructor | IHI | MHI | Chiyoda | Kureha |
| FGD start-up year | 1983 | 1983 | 1982 | 1982 |
| Inlet $SO_2$, ppm | 600-700 | 1000 (900) | 1500 | 1500 |
| Inlet dust, mg/$Nm^3$ | 30-150 | 150 | 180 | 150 |
| 1st scrubber (prescrubber) | Spray | Spray | Venturi | None |
| L/G, liter/$Nm^3$ | 5 | 2 | 1 | - |
| pH | 4.5-5 | 1 | 1 | - |
| 2nd scrubber (scrubber) | Spray | Packed | JBR | P.P.[b] |
| Absorbent pH | 5.5-6 | 5.5 | 5.5 | 5.5 |
| Additive | None | None | None | S.S.[c] |
| L/G, liter/$Nm^3$ | 15 | 20 | - | 2.7 |
| Outlet $SO_2$, ppm[d] | 30-35 | 40 (36) | 35 | 5 |
| Outlet dust, mg/$Nm^3$ [d] | 10-20 | 45 | 25 | 75 |
| $SO_2$ removal, %[d] | 95 | 96 | 98 | 99.7 |
| Dust removal, %[d] | 70-80 | 70 | 78 | 50 |
| $CaCO_3$ utilization, %[e] | Over 99 | Over 99 | Over 99 | Over 99 |
| $H_2SO_4$ consumption, liter/h | 10 | 15 | None | None |
| Wastewater, $m^3$/h | 25 | 15 | 1.5 | 0 |
| Gas reheating | GGH[f] | GGH & SGH[g] | None | None |
| Pressure drop, mm $H_2O$ | 350[h] | 300 (250)[i] | 600 | 200 (170) |
| Power consumption, % | 2.1[h] | 2.0 (1.7)[i] | 1.3 | 1.4 (1.3) |
| Plant cost, yen/kW | 20,000[h] | 21,000[i] | 18,000 | 19,000 |

[a] Oil = 90: Coal = 10, on calorie basis

[b] Perforated plate

[c] Sulfosuccinate

[d] At scrubber outlet

[e] By scrubbers

[f] Gas-gas heater to 100C

[g] Steam-gas heater to 120C

[h] Including GGH

[i] Including GGH and SGH

was put into operation in May 1982. The process is characterized by the use of a single reactor containing gypsum slurry at pH of nearly 4 into which flue gas is injected through many nozzles, limestone powder is added, and air is introduced for oxidation. The plant has no slurry recirculation pumps, resulting in a low power consumption. The plant cost is also low. A continuous centrifuge (super decanter) is useful because gypsum crystals grow very well. The plant has been operated without trouble. Although a small amount of scale forms on some of the gas pipes, the scaling did not hinder its continuous operation for more than a year. Chiyoda has been constructing a similar unit for Chita Oil Co. and units for two 200 MW coal-fired boilers (Table 2).

Kureha Chemical modified the acetate lime gypsum process and has developed the sodium sulfosuccinate limestone process, which has been applied to the Sendai plant of Toyo Rubber Co. (Table 4). Actually anhydrous maleic acid is added to the scrubber liquor, which readily reacts with sodium bisulfite to form sodium sulfosuccinate. The role of the sulfosuccinate may be similar to that of adipic acid used in the U.S.A. Kureha claims that the decomposition rate of the sulfosuccinate is slower than that of adipic acid, and that the decomposition products of the sulfosuccinate give no odor while those from adipic acid may give some odor. The Sendai plant has no prescrubber and gives no wastewater at all. The plant has been operated with over 99% reliability. Power consumption is low because of the small L/G ratio and low pressure drop.

## 4. $NO_x$ Control Systems

Extensive combustion modifications have been applied in Japan to lower $NO_x$ from boilers to 160-400 ppm for coal, 60-130 ppm for oil, and 40-80 ppm for gas to meet the emission standards by the Central Government. In many regions, however, more stringent regulations by local governments require further $NO_x$ reduction. Many plants utilizing SCR of $NO_x$ have been constructed, as shown in Figures 3 and 4. These plants convert $NO_x$ to $N_2$ by treating with $NH_3$ at 300-400C in the presence of a catalyst:

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O$$

Nearly all of the SCR plants constructed before 1977 are for oil-fired industrial boilers and furnaces, while nearly all of the plants constructed since 1978 are for utility boilers. By the end of 1983, the total SCR capacity will reach 60 x $10^6$ $Nm^3/h$ (27,000 MW equivalent), of which about 80% is for utility boilers. By the end of 1985, the total SCR capacity for utility boilers will reach 73 x $10^6$ $Nm^3/h$ (33,000 MW), of which 60% is for oil, 21% for coal, and 19% for gas. The SCR capacity for coal-fired boilers will increase fairly rapidly because most of the new coal-fired utility boilers will need SCR (Figure 4).

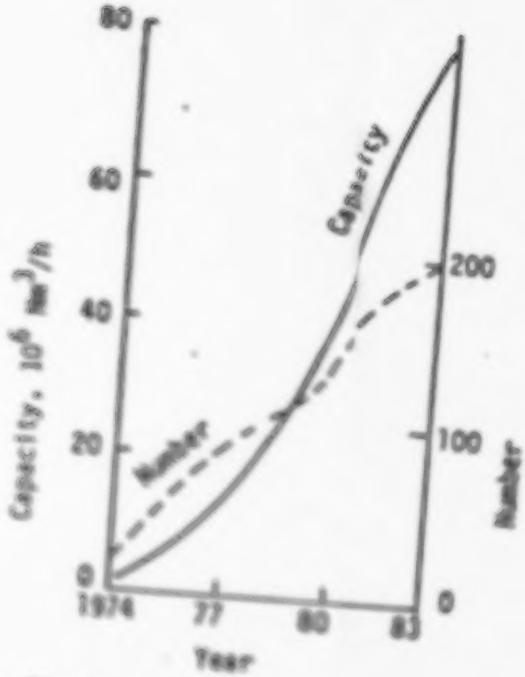


Figure 3. Number and capacity of SCR plants.

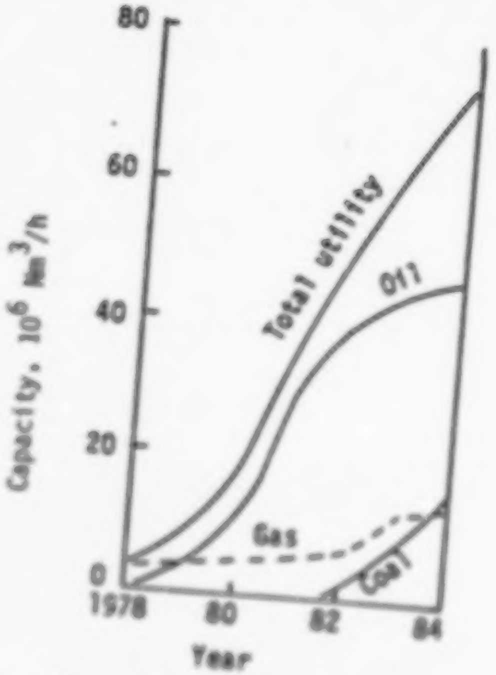
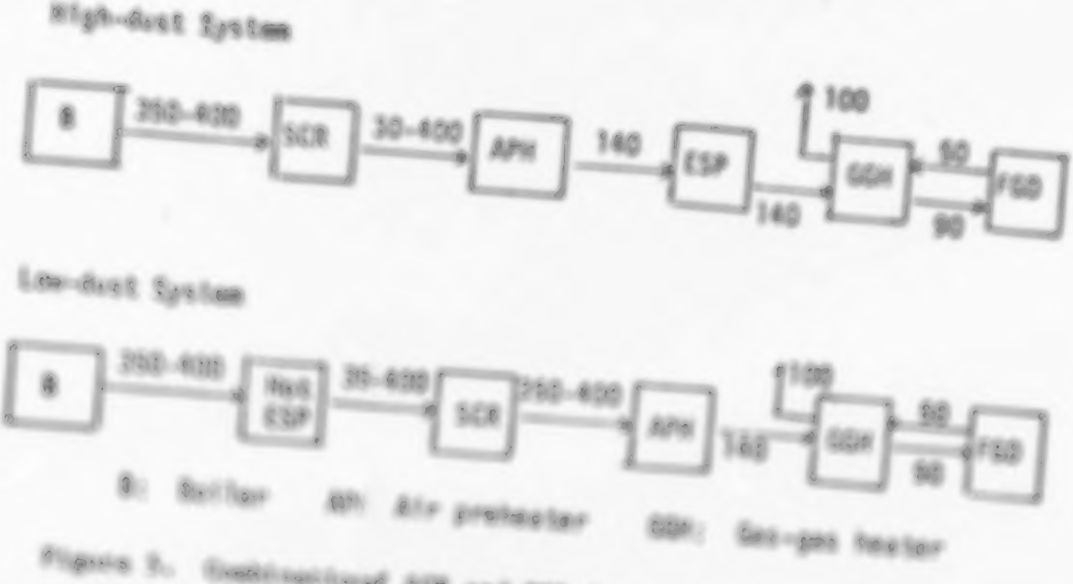


Figure 4. Capacity of SCR plants for utility boilers.



B: Boiler AH: Air preheater GGH: Gas-gas heater

Figure 5. Combinations of SCR and FGD for coal-fired boilers (Figures are gas temperatures, °C).

SCR units for coal-fired boilers are shown in Table 2. Most of the units treat a flue gas from boiler economizer with full dust load at 350-400C (high-dust system, Figure 5) and remove 55-80% of $NO_x$ to meet the regulations, using 0.56-0.83 mole $NH_3$ to 1 mole NO. Plant operation is easy and free of trouble. Three of the plants treat the flue gas after particulate removal by a hot-side ESP (low-dust system, Figure 5). The low-dust system has a slight tendency to deposit dust on the catalyst and ammonium bisulfate in the air preheater, but the system may be operated continuously for 1 year by applying soot blowing. Nearly all of the SCR plants for coal-fired boilers have been constructed by Mitsubishi Heavy Industries and Babcock-Hitachi using honeycomb catalyst and plate catalyst, respectively. The catalyst life may be over two years for coal.

The cost of the SCR plant for utility boilers (yen/kW) for 80% $NO_x$ removal is 6000-8000 for coal, 4000-6000 for oil, and 2500 for gas. The annualized operating cost (yen/kWh), including 7 years depreciation, is 0.5-0.8 for coal, 0.3-0.4 for oil, and 0.2 for gas.(3)

## 5. Combined $SO_2$/$NO_x$ Removal (SCR/FGD Combination)

A combination of FGD and SCR has been applied to industrial boilers and furnaces since 1975 (Table 5) and to coal-fired boilers since 1980 (Table 2). The types of combinations for industrial use are shown in Figure 6.

TABLE 5. COMBINED FGD/SCR PLANTS FOR INDUSTRIAL USE

| Owner | Site | Gas Source | Capacity $Nm^3/h$ | FGD | SCR | Year Completed |
|---|---|---|---|---|---|---|
| Shindaikyowa Petrochem. | Yokkaichi | Oil-fired boiler | 430,000 | MKK-Wellman [illegible] | Hitachi Zosen | 1975 |
| Kawasaki Steel | Chiba | Sintering machine | 762,000 | MHI Lime-gypsum | Hitachi Zosen | 1976 |
| Nippon [illegible] | Kawasaki | Oil-fired boiler | 12,000 | Sodium scrubbing[a] | MKK[b] | 1976 |
| Nippon Kokan (NKK) | Keihin | Sintering machine | 1,[illegible],000 | NKK ammonia scrubbing | NKK | 1979 |
| Tokyo Metropolis | [illegible] | Incinerator | 100,000 | Sodium scrubbing[a] | Mitsui Engineering | 1979 |

[a] Throwaway liquor

[b] Mitsubishi Kakoki Kaisha

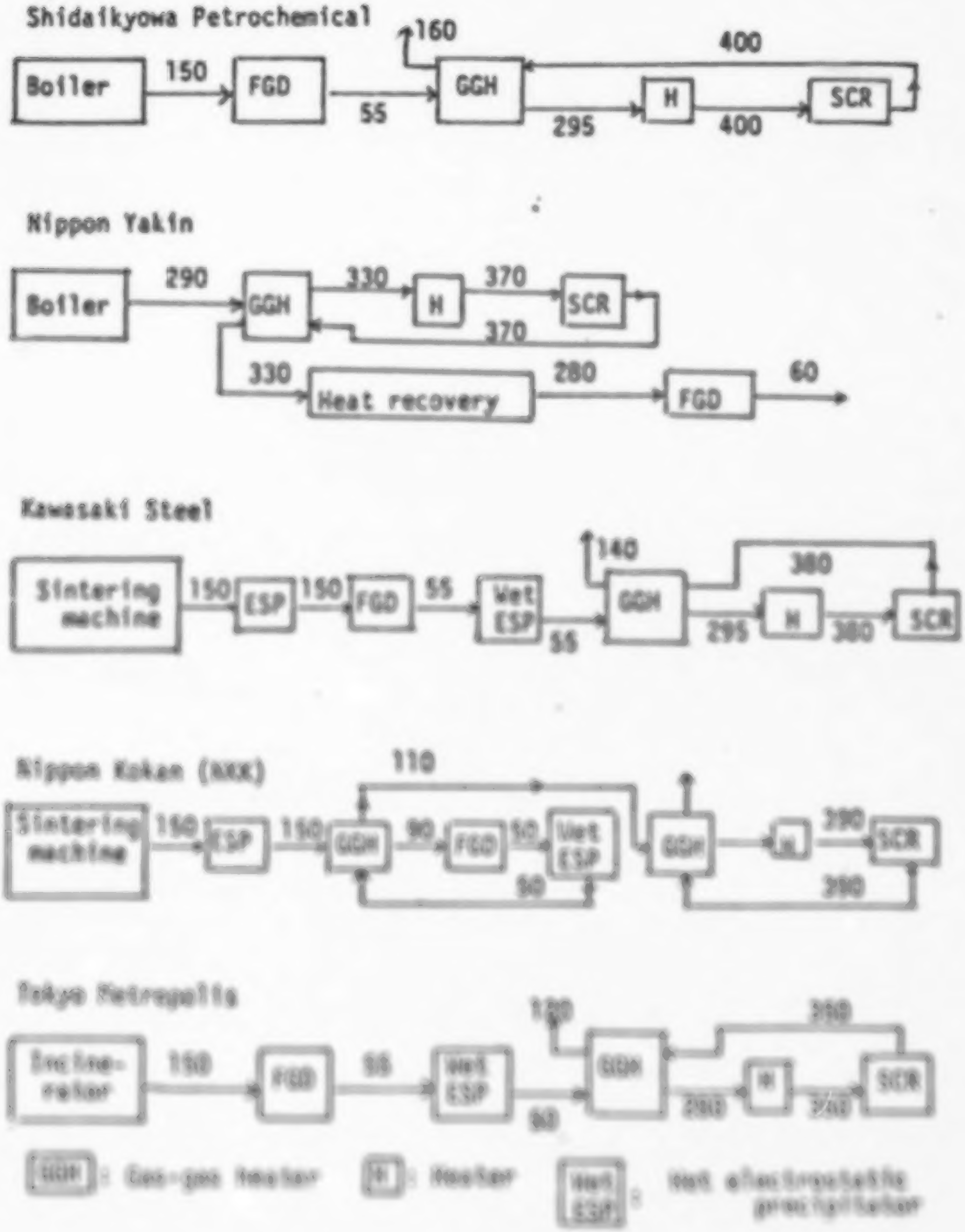


Figure 6. FGD/SCR combinations for industrial use (Figures show gas temperature, °C).

The first plant for an oil-fired boiler was completed in 1975 for Shindaikyowa Petrochemical at Yokkaichi. The plant treats the flue gas first by wet FGD and then by SCR. This FGD/SCR combination is no longer used for boilers because the system requires large amounts of fuel oil for heating and still has an ammonium bisulfate problem with the gas-gas heater.

Nippon Yakin's Kawasaki plant treats flue gas first by SCR and then by FGD. This system is simpler and requires less energy, although a little gas heating is needed because the gas temperature is 290C at the boiler outlet. The SCR unit first used a ring catalyst in a random packing, which caused dust plugging; this was changed to a parallel-flow catalyst in 1978. The combined system has since been operated without trouble, reducing $NO_x$ from 200 to 35 ppm, $SO_2$ from 1000 to 50 ppm, and particulate from 200 to 40 mg/$Nm^3$. The new catalyst has been in use for over 4 years. The plant cost in 1976 was 63 million yen for FGD and 73 million yen for SCR with the heaters. The operation cost, including 7 years depreciation, is about 14,000 yen/kl of heavy oil. Since heavy oil and kerosene currently cost 50,000 yen/kl and 70,000 yen/kl, respectively, giving a 20,000 yen/kl difference, the use of heavy oil with the combined cleaning system is more advantageous than using kerosene without gas cleaning.

Sintering plants of Kawasaki Steel and Nippon Kokan, as well as an incinerator of Tokyo Metropolis, have combined wet FGD, wet ESP, gas heater, and SCR (Table 5 and Figure 6). The temperature of the flue gas from the sintering machines is about 150C. A low-temperature SCR catalyst is not useful for gas because of the high $SO_x$ concentration which causes ammonium bisulfate to deposit on the catalyst. The flue gas from the incinerator is also too dirty to be treated directly by SCR. Therefore, the flue gases are first treated by FGD and wet ESP and the cleaned gases are heated and subjected to SCR.

The Chiba plant of Kawasaki Steel, using lime-gypsum process FGD and a pellet catalyst for SCR, reduces $SO_x$ from 300 to 10 ppm, $NO_x$ from 230 to 20 ppm, and particulates from about 300 to below 10 mg/$Nm^3$.* The catalyst was used for 4 years before it was replaced with a new catalyst which works at a lower temperature for energy saving.

At Nippon Kokan's Keihin plant, $SO_2$ in the sintering machine flue gas is combined with $NH_3$ in coke oven gas to by-produce ammonium sulfate. For SCR, a special iron ore is used as the catalyst in a moving bed. By the combined cleaning, $SO_x$ is reduced from 230 to 70 ppm, particulate is reduced from 300 to 3 mg/$Nm^3$, and $NO_x$ is reduced from 200 to 40 ppm. The investment cost for the SCR plant was [illegible] billion yen including the gas-gas heater and a direct-fired heater.

The combined systems for the sintering machines have been operated without trouble, although the operation cost may be high because a large amount of energy is required for gas heating.

At the Sunamachi plant of Tokyo Metropolis, flue gas from the city waste incinerator is first subjected to sodium scrubbing and then to wet ESP, gas heating, and SCR. A special honeycomb catalyst with a special composition is used to remove odor together with $NO_x$.(3) The plant has been operated without trouble, removing over 90% of $SO_2$ and $NO_x$ with about 80% of the odor. The SCR unit cost 480 million yen, including the gas-gas heater and a direct-fired heater. The SCR cost is about 0.45 yen/$m^3$ of the gas including 10 years depreciation. About 50% of the cost is for fuel for heating. Several similar plants are to be constructed by Mitsui Engineering for incinerators.

For coal-fired boilers, economizer outlet gas at 350-400C is subjected to SCR and then to air preheater and FGD (Figure 3). Possible problems with the cleaning system are contamination of fly ash by ammonia for the high-dust system, ammonium bisulfate deposit in the air preheater for the low-dust system, and contamination of wastewater from FGD by ammonia for both systems. Those problems have been solved by keeping ammonia at the SCR reactor outlet below 5 ppm. Wastewater from FGD plants for coal-fired boilers without SCR usually contains 100-600 mg/$m^3$ of nitrogen in the forms of nitrate and others derived from $NO_x$ in the flue gas. With SCR, a small amount of ammonia goes into wastewater but total nitrogen content seems to be lowered, possibly because of the substantial reduction of nitrogen compounds derived from $NO_x$ in the flue gas.(4)

## 6. Simultaneous $SO_2$ and $NO_x$ Removal

Various simultaneous $SO_2$ and $NO_x$ removal processes were tested between 1975 and 1979 when the combined SCR/FGD system was considered not feasible. Several small commercial units were constructed using wet simultaneous processes by-producing nitrates and sulfates. The simultaneous removal processes, however, have difficulties (including economic disadvantages) and have become less attractive as the combined SCR/FGD system has been commercialized. The above wet processes produce large quantities of waste by-products which would present major problems in Japan if applied on a large scale. Wet processes by-producing elemental sulfur along with ammonia or $H_2$ were tested, but seem too complex for commercial application.

Some dry simultaneous removal processes were also given up because of their high cost. However, two dry simultaneous removal processes, activated carbon and electron beam, are to be further developed aiming at commercial application. A demonstration plant of the activated carbon process, with a capacity of treating 300,000 $Nm^3$/h of flue gas from a coal-fired boiler, is under construction at Matsushima Station of EPDC to remove over 90% of $SO_2$ with a 20-40% reduction of $NO_x$. The plant will by-produce elemental sulfur by reducing the recovered concentrated $SO_2$ in a reactor containing coal and Claus furnaces. For commercial use, very cheap carbon is needed because of the high carbon consumption. The electron beam process, by-producing ammonium sulfate and nitrate, may not be suitable in Japan where ammonium sulfate is in oversupply and the nitrate has little use. The process may be useful in a country which has a demand for the sulfate and nitrate for fertilizer, if a large electron beam accelerator is commercialized for a reasonable cost.

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## PANEL: THE ARCHITECT-ENGINEER - MIDDLEMAN BETWEEN UTILITY AND FGD SUPPLIER

Chairman: A. V. Slack
President
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# Panel Discussion. The A&E - Middleman Between Utility and FGD Supplier

BY: E.W. Stenby

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## ABSTRACT

The A-E is hired to represent the owner through all phases of a scrubber system selection and installation. In this capacity, the A-E is expected to exercise good judgement in the areas of design and cost. The owner, depending on the size of his staff and his experience, may leave all or most decisions to his A-E or he may participate a great deal. We feel it is very important that the owner participate fully in all aspects of the scrubber system design and installation, since he will be left to operate the system after the vendor and A-E have gone home.

The A-E's objective is to specify and procure the most reliable scrubber system at the low evaluated cost. The scrubber business, however, is highly competitive and the vendor's objective is to win the award, knowing that low cost is one of the primary selection parameters. The document used by all parties to arrive at the appropriate selection is the specification. In Stearns-Roger's opinion, a good spec will detail not only basic design criteria, but also minimum levels of quality in equipment components. materials of construction and equipment sparing philosophy. A very important area is performance guarantees. A conservative spec may tend to drive the capital cost of the scrubber system upwards, but we consider it to be the best means currently of achieving high operating reliability. However, a very detailed spec can conflict with the owner's desire to obtain maximum vendor exposure on equipment guarantees and performance guarantees. By dictating too much of the system detail design, the A-E and owner take some of the risk.

The current fixed price natre of the FGD business forces the vendor to absorb the risk of cost ove-runs. During the proposal stage the vendor usually does minimal enginering to prepare his bid. Under these circumstances there will be a tenency for the successful vendor to protect his profit by calling for an exra, everytime the A-E or owner makes a comment. The vendor will try to minilze or prevent the owner and A-E from interfering with the design and constrution are in conformance with the spec and the intent of the spec. Again,the spec becomes the all important document in interpreting what is requird and what is acceptable. It is absolutely essential, therefore, that good spec be developed.

In order to ensure that a gd proposal be prepared, it is suggested that the

owner consider paying for the proposal. In this manner, vendors will be encouraged to do more engineering and provide better detail of his proposed design. A limited bidder's list goes hand in hand with this approach.

One last thought... it must be remembered that there are many "gray" areas in scrubber design and it is difficult, if not impossible, to get all the details spelled out clearly during the bidding phase. A goal of the A-E is to interpret and help coordinate the owner's requirements into positive action by the vendor during the design and construction phase. The owner also has a resposibility to know what he is buying and to apply standards of operation and maintenance for the scrubber system that are consistent with the rest of the plant.

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## The Role of Engineer-Constructors In Flue Gas Desulfurization

By G. H. Dyer
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San Francisco, CA

### ABSTRACT

First, I would like to note that I have recast the title, since we think of ourselves as being Engineer-Constructors rather than that of an Architect-Engineers. We believe that to be a distinct difference in that it provides an ability to provide a continuity between engineering and construction activities that is vital to the timely and successful completion of jobs involving complex systems.

Second, in the short time available, I would like to concentrate on the Engineering end of this subject.

Lastly, as a representative of the Research and Engineering part of the Bechtel Group of Companies, I would like to explain our views of developmental aspects of Flus Gas Desulfurization as well as its production engineering aspects.

To start off (SLIDE 1) I would like to remind you of the very broad definition of Engineering, as given in standard dictionaries.

Applying this definition to the subject of Flue Gas Desulfurization (SLIDE 2) we can easily come up with a long list of more detailed functions, all or most of which involve Engineering, in the professional sense. In fact, we find people with these talents and experience throughout the various portions of the industry, from the regulatory agencies to process development activities, to equipment suppliers, systems engineers, constructors and plant operators.

The issue I would like to address today, is where these functions should best be performed. I hope to be able to show you that this question is

SLIDE 1

ENGINEERING!

THE APPLICATION OF SCIENCE AND MATHEMATICS BY WHICH THE PROPERTIES OF MATTER AND THE SOURCES OF ENERGY IN NATURE ARE MADE USEFUL TO MAN IN STRUCTURES, MACHINES, PRODUCTS, SYSTEMS, AND PROCESSES.

A. MERRIAM-WEBSTER

SLIDE 2

## PROFESSIONAL ENGINEERING SERVICES REQUIRED

| | |
|---|---|
| REGULATORY | - ESTABLISH NEEDS, REGULATIONS, MONITOR RESULTS |
| PROCESS DEVELOPMENT | - CONCEPTION, DEVELOPMENTS, SCALE-UP |
| SYSTEMS ENGINEERING | - SYSTEMS CONCEPT (FGD VERSUS COAL SELECTION, CLEANING)<br>- FGD PROCESS FLOW SHEET<br>- EQUIPMENT SELECTION AND PROCUREMENT<br>- AUXILIARIES<br>- DETAILED DESIGN FOR CONSTRUCTION |
| EQUIPMENT MANUFACTURING | - DESIGN, FABRICATE, TEST |
| CONSTRUCTION | - METHODS<br>- CRAFT SUPERVISION<br>- INSPECTION, QUALITY CONTROL<br>- START-UP, SYSTEMS MANUALS, TRAINING |
| OPERATION | - TECHNICAL SUPERVISION<br>- REPAIR, MAINTENANCE |

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answered differently for differing industries, differing kinds of technology, and for different stages of technology development, and that the technical nature of Flue Gas Desulfurization is sufficiently different from the rest of the technology used by the electric utility industry so as to suggest valid differences in how the related engineering should be conducted.

In presenting this thinking, I should also state that there is no single method which is best under all conditions. We do projects under many different circumstances, and our project people are given a substantial degree of freedom to structure their projects as they see fit for their specific circumstances. If there is any hard Bechtel policy on the matter, it is only that this flexibility shall be maintained.

First, I would like to suggest some principles (SLIDE 3) that are generally true, regardless of the type of industry involved. Fundamental to these is the notion that the ultimate plant owner/operator must maintain control. To exercise this control he should staff with his own engineering support capabilities to the extent that he can do so without creating problems for himself, that is, either creating conflicts, or what I will call Inefficiencies.

A typical conflict is that the regulatory engineers must not be on the owner's staff, for there would be a clear potential for conflict of interest. However, the owner should have people available who can work closely with them.

There are also some conflicts with which the electric utility industry is not generally familiar. These are due to the tightly held proprietary positions that are maintained in some highly competitive industries, such as the pharmaceutical industry. As a result, almost all engineering is done in-house and only non-proprietary related activities are conducted by others.

Beyond these conflicts, the main inefficiency seen by most owners has to do with the cyclic demands for engineering support - which are dependent upon the nature of their capital plant additions. In the pharmaceutical industry, most expansions are small, or are modifications to existing systems, and are done by in-house engineers on a relatively steady state of employment level. In the refinery and chemicals business there are similarities, and strong owner engineering staffs, with outside assistance requested only for their larger projects. In the electric power business, additions are usually made in larger single steps, tending to present an increased cyclic staffing level problem, and increased incentives to obtain outside support to avoid major in-house staffing level cycles. I believe these principles are well understood.

Another major factor in efficiently utilizing a particular engineering talent is to consider the necessary inputs and feedback that an engineer needs in order to do his job. Clearly, an engineer who is designing an impeller for a pump needs all kinds of interactions with laboratory tests on various fluids, as well as with those who make castings and machine metal parts. It would be inefficient to locate such an engineer at an electric utility site.

Thus, in the evolution of our businesses we have properly consigned this general class of engineering activity to the equipment manufacturers site.

The same logic can be used for other classes of engineers, but with perhaps differing results. As a case in point, the systems engineer, the one who puts several component parts into an operating process or system, should be located at, and have his feedback derived from the site that has the greatest involvement in the development and use of the system. For pharmaceutical plants these engineers are clearly located in-house within the operating company, due both to secrecy and efficiency aspects. In refinery and chemical plants, there tends to be a mix, with some proprietary systems packages produced by organizations such as UOP, and with other state-of-the-art systems being developed by either in-house engineers - or by outside engineering assistance if workload fluctuations are important. In these cases, there are often many interties between the various systems requiring that the plant owners engineers design the overall system and then procure separate chemical unit operation components of known performance value and assemble them into a system using well proven and previously demonstrated engineering principles.

In electric utility plant design, the systems engineer of the past also did the same thing. However, the number of components was smaller, and each tended to be centrally manufactured elsewhere. Thus a system of major equipment might have included separate components for coal pretreatment, boilers, turbines, generators, and power transmission systems, and the owners systems engineer was more involved in their selection and erection than he was in their internal technology development.

SLIDE 3

o OWNER CONTROL

o EXCEPTIONS

1. CONFLICTS - REGULATORY
   - TIGHTLY HELD SECRETS
2. INEFFICIENCIES - CYCLIC STAFFING NEEDS
   - EXPERIENCE FEEDBACK
   - SYSTEMS INTERTIES

When a new technology is being first developed, it is even more important that the engineer be located at the site where the development of the technology takes place (SLIDE 4). In the case of Flue Gas Desulfurization this development took place in two diverse ways. First, the EPA sponsored development work at the Shawnee Test Facility. Secondly, numerous private organizations saw an opportunity for new business and proceeded with their own separate development programs. Since the EPA program was paid for by the taxpayers, that technology has became open-art, while the privately developed technology became proprietary to its developers. However, for lime/limestone processes, with some exceptions, Shawnee really showed the basic chemistry while the other developments have been more oriented to the further development of individual components of equipment to better handle a particular unit operation, such as nozzle spray patterns and gas distribution, vessel designs and mist elimination.

Now that the technology of Flue Gas Desulfurization has generally matured, we believe that process, or chemistry related, guarantees are becoming of lesser importance. This, of course, does not diminish the importance of assuring the quality of workmanship and viability of individual components which must continue in order to deliver the expected process performance over the life of the plant. However, since Flue Gas Desulfurization is really a series of chemical unit operations, including potential interties into other power plant sub-systems involving heat and water utilization and waste solids rejection, we believe that the system tends to start looking more like a refinery and that the owner's engineer - or his contract engineer - should be in firm charge of designing the systems involved. Inherently, as it has elsewhere, this will also tend to place less emphasis on the use of externally supplied systems packages.

The developmental operation of Bechtel, which I represent, recognized the probable evolution of these circumstances a number of years ago. As a result, we sought out, and were pleased to have the opportunity, (SLIDE 5) to play a key role in the basic development of lime/limestone Flue Gas Desulfurization technology by designing, and then performing as the test director for the EPA Shawnee Alkali Flue Gas Desulfurization Test Facility. This gave us an unusual early insight into the basic chemistry as well as many of the requirements for the equipment required to handle these chemical engineering unit operations.

We were also fortunate to have the opportunity to work on Colstrip Units 1 & 2, and were able to improve the system's concept by removing both sulfur and particulate removal in a single set of venturi scrubbers, and in doing so we were able to recover and utilize the alkalinity that inherently existed in the fly ash - thus avoiding the use of extensive additional alkali feed material.

We were also given another unusual opportunity on Colstrip 3 & 4, which needed much higher $SO_2$ removal than Units 1 & 2, to develop a method for the use of a more reactive alkali, Type S Lime. This systems approach, aided by seal water pump packings that require much less water, have now allowed us to

SLIDE 4

## FLUE GAS DESULFURIZATION TECHNOLOGY DEVELOPMENT

- EPA
    - CHEMISTRY/PROCESS
- PRIVATE
    - PROPRIETARY COMPONENTS
- MATURE
- GUARANTEES
    - PROCESS
    - COMPONENTS
- CHEMICAL UNIT OPERATIONS
    - SYSTEMS INTERTIES
- OWNER SYSTEMS ENGINEERING

SLIDE 5

## BECHTEL ROLES IN FLUE GAS DESULFURIZATION DEVELOPMENT

- SHAWNEE
    - DESIGN
    - TEST DIRECTION
- COLSTRIP 1 & 2
    - NO ESP
    - ALKALINE ASH UTILIZATION
- COLSTRIP 3 & 4
    - REACTIVE TYPE S LIME
    - WASTE WATER SINK
- SPRAY DRY
    - REACTIVE TYPE S LIME

make the Flue Gas Desulfurization system a waste water sink instead of a source, with a variety of other plant waste streams being evaporated in the scrubber. Colstrip Units 3 & 4 will both employ these systems, with Colstrip Unit 3 starting up this month.

We have also used these systems insights as a basis to further develop, and pilot test, technology to allow spray dry Flue Gas Desulfurization systems to use much more reactive reagents, with substantial reductions in the resulting equipment size, elimination of recycle requirements, and use of spray dry equipment on high sulfur coals as well as on low sulfur coals while obtaining high $SO_2$ removal.

Lastly, we are also fortunate to be substantially involved in new process developments for precombustion sulfur removal, including advanced coal cleaning technology and the use of coal water mixtures.

It is equally important to note that, at least for our utility applications, we view all of the above systems engineering as non-proprietary open-art technology. We do not charge license fees to our utility clients, nor do we limit our consideration of applicable process systems to that which we may have developed, or assisted in its development. Rather, we believe it is the engineer's job to continue to remain unfettered by commercial interests and to be free to select, and design, the combination of processes that best suits any particular owner for that particular owners specific site related needs and opportunities.

In summary, (SLIDE 6) we believe that the technology has now reasonably matured to a level where the utility needs to place greater emphasis upon component quality rather than process performance guarantees, that much of the technology is based upon open-art chemical engineering unit operations, and that, because of the numerous interties that are necessary with the rest of the utilities system, the utility owners should start to place more emphasis on control over the engineering - either through additions to their own staff or by increased use of contract engineering services.

SLIDE 6

SUMMARY

TECHNOLOGY HAS MATURED

PERFORMANCE GUARANTEES

- COMPONENTS VERSUS PROCESS

CHEMICAL UNIT OPERATIONS

- OPEN-ART
- SYSTEMS INTERTIES

OWNER CONTROL OF SYSTEMS ENGINEERING

## THE ARCHITECT-ENGINEER -- MIDDLEMAN BETWEEN UTILITY AND FGD SUPPLIER

Opening remarks by: P. R. Predick
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### ABSTRACT

Architect-Engineers (AEs) should serve as an extension of a utility's engineering staff to procure an economical FGD system which provides compliance with the applicable emission limits. To this end, AEs prepare design criteria, write specifications, evaluate bids, administer contracts and coordinate equipment interfaces. Sargent & Lundy's recommendations for the procurement of a successful FGD system are summarized, and suggestions are provided to illustrate these recommendations.

## OPERATING EXPERIENCE FEEDBACK

by: Michael L. Meadows, P.E.
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### ABSTRACT

One of the important activities in which the architect/engineer (A/E) serves as an intermediary between the utility and the flue gas desulfurization (FGD) system supplier is preparation of equipment purchase specifications. One of the A/E's many goals in preparing this procurement document is to ensure that the bid specification requirements reflect current knowledge gained from operation of existing FGD systems. Accurate and detailed information about operating experiences at utility FGD systems is difficult and time consuming to collect, but it is one of the best methods for improving FGD system reliability and maintainability. As part of an effort to improve the availability of operating FGD system experience information, Black & Veatch has participated in several recent projects sponsored by the Electric Power Research Institute to assist the utility industry. These projects have included:

- Lime FGD Systems Data Book (Second Edition, CS-2781).
- Limestone FGD Systems Data Book (CS-2949).
- Operation and Design of Dampers in FGD Systems (RP-2250-1).
- FGD Systems Spare Parts Program Practices (RP-2248-4).

In addition, Black & Veatch is participating with Los Angeles Department of Water and Power and the FGD equipment supplier in an Availability Improvement Program for the new 1,500 MW Intermountain Power Project. This task force has made recommendations on many facets of the FGD system now under design which are intended to improve the reliability of the system. A significant portion of this effort has included visits to several operating FGD systems to evaluate and discuss the strengths and weaknesses of their systems.

# THE ARCHITECT/ENGINEER - MIDDLEMEN BETWEEN UTILITY AND FGD SUPPLIER

Douglas B. Hammontree, P.E.
Burns & McDonnell

## ABSTRACT

In administering the FGD system contract, as with any contract throughout the plant, the A/E must maintain a professional relationship with the vendor, remaining impartial and committed to their interests. On the other hand, keep in mind that we are hired and paid by the utility. At Burns & McDonnell we act as an extension of the Owner's staff and we are totally dedicated to the Owner's interests and needs.

I mention this to clarify our role as middleman and to shed some light on the discussion of the problems encountered in this role. Hopefully, with a good specification, the intermediary role is minimized. No problems should develop unless deviations to the specifications occur.

But, of course, problems do occur. Nozzles plug, valves don't seal, materials corrode, and mist eliminators do not. While these are problems that must be faced, the biggest problem as intermediary is to integrate the FGD system with the power plant itself.

With continuing developments in the FGD industry, current designs have reached the stage where the process is adequate to meet removal efficiencies. Equipment and instrumentation is, for the most part, workable. Problems with materials construction are slowly being resolved. In general, reliability problems of current FGD systems can be traced to lack of operator understanding.

It is this situation in which the A/E as middleman, must provide guidance, both to the utility and the vendor. Typically the utility has extensive experience with the boiler/turbine operation. The FGD system presents them with a chemical process plant "located out back by the stack." The A/E must ensure that the utility is prepared to operate this system. We must let them know what to expect. Maintenance and operation requirements are more extensive than in the plant, and the utility must be made aware so that appropriate staffing needs are met.

Operators must be trained in the chemical nature of the system. They quickly find that mechanical solutions are not always adequate for the problems that arise. As with the boiler, where proper control id required to prevent slagging and poor heat rates, there are certain chemical parameters in the FGD system operation that must be monitored to keep the system operating economically and efficiently. Appropriate training programs are vital to meet this need.

With regard to the FGD system supplier, the A/E's goal as middleman is to ensure that the equipment supplied is compatible with the rest of the powerhouse. Mainteanance and operation personnel will be burdened enough without having to learn about all new equipment can and should be by the same manufacturer throughout. Valve operators, solenoids, limit switches, etc., can be the same. Rather than strict demarktion between powerhouse and FGD system, computer control system should be identical. Logic diagram, flow diagrams and process instrument diagram should be consistent in meaning, with common tag and connection numbering.

By integrating the FGD system in this manner, training and operator understanding will be one step ahead. Process problems will more easily understood and resolved.

The FGD industry is young with slightly more than 10 years' experience in broad application. There will continue to be problems at any intallation. It is the A/E's dutv to ensure that the utility and the FGD supplies are working together to provide for the proper training ind integration required for an efficient and reliable system.

## THE ROLE OF THE ENGINEER/CONSTRUCTOR IN FGD

by: Christopher P. Wedig
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### ABSTRACT

The role of the Engineer/Constructor (E/C) in FGD depends on the contract between the utility and E/C. Usually, the E/C will provide to the utility licensing service, studies, specifications, comparison of bids, purchasing services, review and supervision of FGD supplier engineering and construction. In addition, the E/C provides design and engineering of the electrical, controls, and structural areas, construction, start-up, and maintenance training.

The following represents some of the many important concepts in performing the E/C work for the utility and being the intermediary between the utility and FGD system supplier.

1. Licensing of the coal fired power plant site should be based on proven FGD technologies.

2. FGD and FGD waste studies should be performed in an unbiased manner and based on E/C and utility "inhouse" information plus written correspondence and meetings with FGD and FGD waste system suppliers.

3. The FGD and FGD waste specifications should be a combination performance and design specification. The specification should be a "tool" with which the utility and E/C purchase a highly reliable system. Design parameters should be specified for those areas in which problems have occured in operating systems. The E/C should make frequent visits to operating FGD systems and to manufacturers of components to ensure that he has knowledge of problem areas. Performance acceptance tests, guarantees, and warranties should be emphasized. The specification should be reviewed by the utility engineering, construction, and power production departments.

4. The FGD supplier bidders list should be short and contain only suppliers of proven technology and demonstrated highly reliable operating systems. All FGD suppliers should be treated in an unbiased manner. The bidders should bid to the base specification and offer exceptions or options only when it will improve or not effect system reliability. The award of contract to the FGD or FGD waste system supplier should be based on a present worth total evaluated cost basis which includes all costs of the system supplier, utility, and E/C.

5. The E/C should carry out the utility's directions, while at the same time providing reliable advice. The E/C should ensure that the FGD system equipment is designed similar to the balance of the power plant so that maintenance procedures are compatible and spare parts are minimized. The E/C and utility should review and monitor the engineering and construction work of the FGD supplier. The E/C and FGD supplier should work as a team to ensure that interface problems are minimized. The FGD supplier should engineer and construct in accordance with the system purchase specification and should inform his subsuppliers and subcontractors of the requirements of the purchase specification.

6. The utility, E/C, and FGD & FGD waste system suppliers should work as a team in the start-up and maintenance training of the systems. The utility should train the O&M personnel before the systems become operational and participate in the start-up of the systems. The E/C and FGD supplier should provide start-up services and numerous training classes for the utility O&M personnel. The E/C should ensure that the performance acceptance tests and supplier guarantee/warranty requirements are met in accordance with the

**purchase specification. The FGD supplier should not be permitted to leave the site until he has met all of the requirements of the purchase specification. The E/C and FGD & FGD waste system suppliers should be permitted to work with the utility during the entire life of the systems to provide, on an as needed basis, engineering and training services to ensure a highly reliable FGD and FGD waste system.**

# "THE ARCHITECT/ENGINEER - MIDDLEMAN BETWEEN UTILITY AND FGD SUPPLIER"

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## ABSTRACT

As the "middleman," the architect-engineer has a responsibility, a role and a salient position.

The responsibility of the "A/E" with respect to flue gas desulfurization (FGD) is to define the term "good engineering practices" and apply its principles throughout a project to obtain two fundamental objectives - operational reliability and cost-effectiveness. The responsibility of the A/E with respect to FGD is similar to the A/E's responsibility for other technologies that comprise a steam-electric generating plant. The task of this responsibility with respect to flue gas desulfurization, in comparison to other technologies, is more difficult because of the relatively developmental status of FGD technology and the fact that the utility, architect-engineer and the FGD supplier can not unilaterally design this part of the plant. Regulatory agencies and the general public scrutinize and approve the adequacy of designs.

The role of the A/E is to direct the process by which: (1) a philosophy of design is developed by the utility, (2) the technical issues are identified complete with the proper economic assessment, (3) necessary decisions are made by the utility on a timely basis to meet project objectives, (4) competitive bids are secured that address the technical issues and allow the inclusion of the bidders' expertise and ingenuity, (5) evaluations are conducted in in accord with the aforementioned responsibility, (6) operational results are evaluated to measure achievement.

The position of the A/E enables him to input objective and credible perspectives into the project. The A/E is not subject to the competitive pressures of FGD suppliers. The position of the A/E enables him to perform "power plant engineering" allowing the FGD supplier to concentrate upon the core of the FGD system (the essentials to achieve performance). The A/E's position is a perch from which credible perspectives of the impact of FGD upon the overall plant design, cost and operation can be provided to regulatory agencies and the general public.

Concerning responsibility, the definition of "good engineering practices" enconpasses identifying commercially available technologies commensurate with the planned operation of the particular steam-electric generating unit, establishing the proper degree of redundancy, space requirements and enclosures to allow performance of necessary maintenance, and integrating the FGD operation into the overall power plant operation.

Concerning the role of the A/E, as the director of the engineering process he is the "chief designer." With respect to technical issues, the primary issues are "dry " versus "wet" scrubbing, selection of suitable materials of construction and determining the proper degree of redundancy.

From the developed design philosophy which begins with applying the economic factors to design concepts, technical issues related to the degree of design conservatism and cost can be settled. To the extent that such issues are settled prior to the specification, the burden of bidding by the FGD suppliers is reduced.

Corresponding to the increasing maturity of flue gas desulfurization technology, the position of the A/E has become more significant. Specifications have become more detailed as the impact upon the overall plant operations became more perceptible. The position of the A/E can increase further in stature, if he assumes more responsibility for the "balance-of-plant" aspects of flue gas desulfurization."

## SESSION 7: FGD CHEMISTRY

Chairwoman: Dorothy A. Stewart
Electric Power Research Institute
Palo Alto, CA

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# INFLUENCE OF CHLORIDES ON THE PERFORMANCE OF FLUE GAS DESULFURIZATION

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## ABSTRACT

A pilot plant test program was performed to determine what effect high concentrations of chloride might have on the performance of limestone-based flue gas desulfurization (FGD) processes. This test program took place during January and February 1983 at the Tennessee Valley Authority (TVA) Shawnee Steam Plant. The specter of high chloride concentration arises from a trend toward closed-loop operation. The influence of chlorides on $SO_2$ absorption was examined; 161 limestone tests were completed. The principal conclusion that can be drawn from this test program is that chlorides generally inhibit $SO_2$ absorption. The severity of this effect can vary widely, however, depending upon the design and method of operation.

## INTRODUCTION

One of the most serious concerns of current and future users of lime and limestone-based (L/L) FGD systems involves the influence with which chlorides (and to a lesser extent, fluorides) will affect the performance of these processes. In response to these concerns, Babcock & Wilcox (B&W) approached the Tennessee Valley Authority (TVA) in May 1982 to solicit interest in a joint pilot plant project at TVA's Shawnee pilot plant facilities. TVA's interest concerned limestone flue gas desulfurization (FGD) systems, whose closed-loop water operations could be subjected to high chloride concentrations.

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Prepared for presentation at Environmental Protection Agency/Electric Power Research Institute Symposium on Flue Gas Desulfurization, New Orleans, La., November 1 - 4, 1983.

Subsequently, the Electric Power Research Institute (EPRI) joined the project and participated in developing a pilot plant test program to study the influence of high chloride concentrations on $SO_2$ absorption. Two objectives of this test program included:

- To determine to what extent chloride would influence $SO_2$ absorption if chlorides were permitted to build up to concentrations as high as 60,000 ppm in the recirculation loop.
- To investigate whether certain system design parameters were capable of reducing harmful effects of chloride.

An implicit objective of this test program was to evaluate to what extent heterogeneous (liquid/solid) reactions take place within the absorber and to what extent they might alleviate reductions in $SO_2$ absorption that could result when chlorides are added to calcium-based slurries.

## PILOT PLANT FACILITIES

TVA's pilot plant facilities at the Shawnee Steam Plant include most of the elements common to full-scale, limestone, FGD systems. The main facilities utilized for this test program included a 30,000-ACFM pilot plant, designated by TVA as Train 200, and a dry limestone preparation facility for grinding limestone to desired fineness.

Some modifications to Train 200 were made for this test program. These included installing a venturi scrubber placed ahead of the pilot absorber, as well as modifications to the absorber itself. The venturi scrubber was installed to remove fly ash from the flue gas via a water spray. The absorber is a square tower with a flow area of about 31 $ft^2$ that was originally designed to simulate a Turbulent Contact Absorber. This absorber was modified for these tests to simulate B&W's L/L absorber with B&W sieve trays.

In addition to these changes, an $SO_2$ vaporizer/injection system was installed to permit variability in $SO_2$ concentration in the flue gas.

## BACKGROUND

Currently, most operating L/L FGD systems experience chloride levels in the range of 2000 to 8000 ppm. In this range, few process-related problems have been experienced. However, some architect/engineers anticipate future FGD systems to far exceed these levels (30,000 to 120,000 ppm, for example). How this could develop is best shown by considering a simplified power plant flowsheet (Figure 1). Chlorides enter these systems with coal and fresh water makeup. Chlorides have the property of being easily and completely dissolved in water. The only escape for chlorides from these water cycles depicted in Figure 1 is via cooling tower blowdown and with the free moisture that leaves with the scrubber sludge. Typically, for every 1 pound of coal that is burned in the boiler, about 4 pounds of water are evaporated in the cooling tower, and 1/2 pound of water is evaporated in the scrubber. Eastern bituminous coals average about 800 ppm chlorides. Therefore, if the water contains about 100 ppm chlorides in this generalized example, then each pound of coal will result in the addition of about $1.25 \times 10^{-3}$ pound of chlorides.

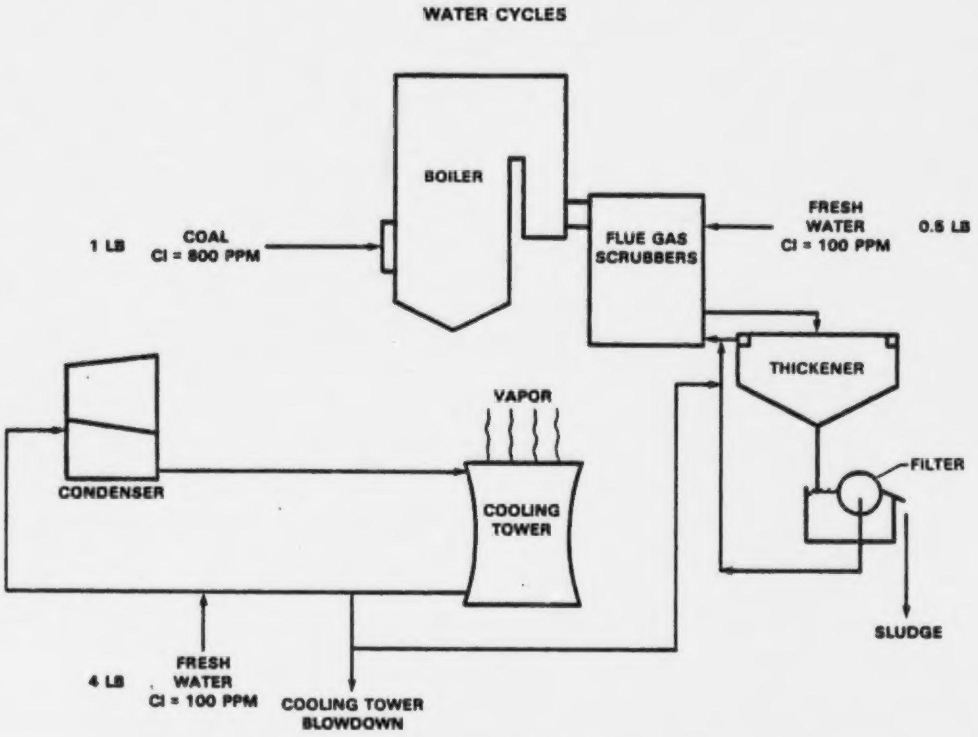


Figure 1. Simplified power plant back-end flowsheet.

Since blowdown from the cooling tower can be ecologically undesirable, and since every pound of blowdown water requires an additional pound of precious fresh water makeup, it is in the utilitys' interest to minimize that blowdown. This fact provides motivation to use blowdown water as the principal source of water in the FGD system. This reduces the demand of the FGD system for fresh water and reduces the amount of cooling tower blowdown.

Take this example to its extreme. If all cooling tower blowdown is directed to the FGD system, then the steady-state chloride concentration can be shown [1] to depend only on the degree of sludge dewatering (Figure 2). The fact that industry trends point toward both water conservation and improved sludge dewatering brings into focus the concern over chlorides.

A major concern regarding chlorides in the electric utility industry is the implication that catastrophic corrosion could occur even with the use of expensive alloys. As important as this concern is, however, the mission of this project was not to explore the implications of chloride buildup upon materials of construction. The literature is crowded with corrosion studies as applied to FGD processes and is not repeated here.

Although the concern for chloride buildup is relatively recent as it applies to FGD processes in the electric utility industry, chloride buildup in various pulp and paper processes has been a problem of concern for many years. Two methods used to remove chlorides in the pulp and paper industry are discussed by Karjalainen, et al. [2] and Reeve, et al. [3].

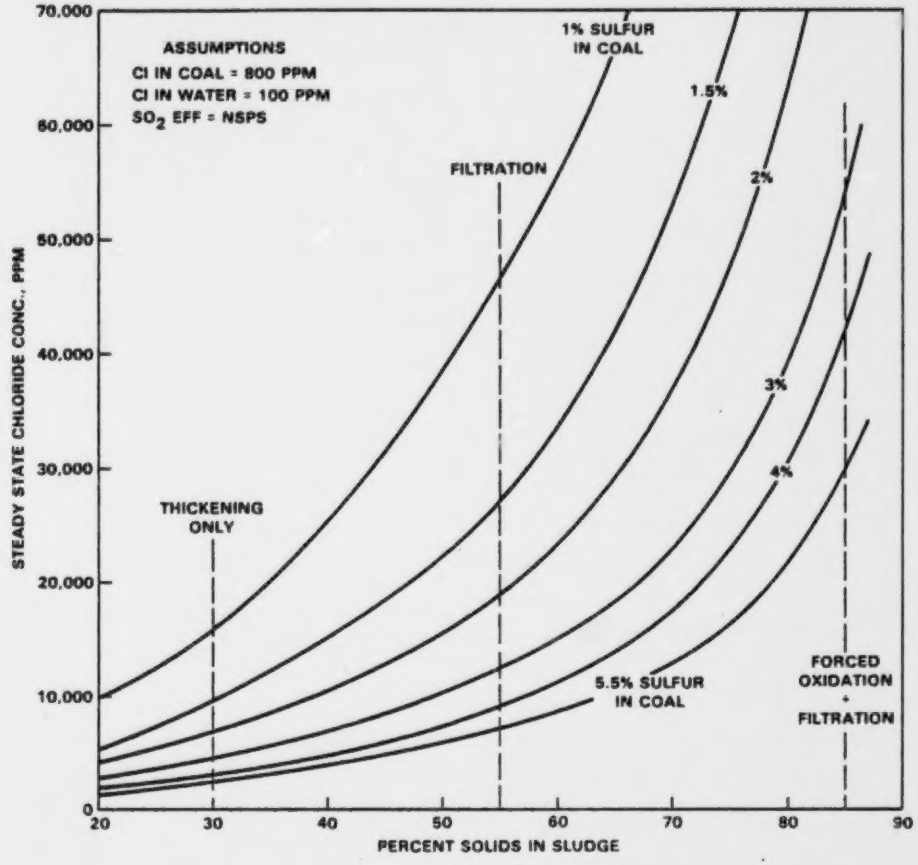


Figure 2. Chloride levels achievable in closed-cycle operation.

Studies dealing with the implication of chloride buildup in FGD systems are relatively recent. Much of the current interest in chlorides arises from the fact that results reported in the past few years (1971 - 1981) have been varied, inconsistent, and confusing. Bechtel [4] and Rader [1] reported that $SO_2$ absorption improved slightly with increasing chloride concentrations up to about 20,000 ppm. Others, notably Chang and Laslo [5], reported a very substantial decrease in $SO_2$ absorption at chloride concentration ranges up to 180,000 ppm. To complete the trilogy, Rader [6] reported on an expanded pilot plant test program at higher chloride concentrations (up to 80,000 ppm) and showed that chlorides had no significant effect on $SO_2$ absorption.

The fact that all these observations were made at various times on different pilot plants is testimony to the complex interaction and trade-offs that contribute to the performance of lime/limestone scrubbers.

The most obvious influence of chlorides in the FGD system is to decrease the solubility of calcium salts because of the "common ion effect." This situation results when HCl produced in the furnace from the chloride in the coal is collected in the absorber by, for example, the following simplified reaction:

$$2\ HCl_{(g)} + CaCO_{3(s)} \longrightarrow CaCl_{2(aq)} + H_2O + CO_{2(g)} \qquad \text{(R1)}$$

Thus, dissolved calcium ion ($Ca^{++}$), builds up in proportion to the chloride concentration that, in turn, limits the solubility of basic species via:

$$(CO_3^{=}) = \frac{K_{sp\ 1}}{(Ca^{++})} \qquad \text{(E1a)}$$

$$(SO_3^{=}) = \frac{K_{sp\ 2}}{(Ca^{++})} \qquad \text{(E1b)}$$

$$(SO_4^{=}) = \frac{K_{sp\ 3}}{(Ca^{++})} \qquad \text{(E1c)}$$

The result of this common ion effect is to reduce the dissolved alkalinity of the scrubbing slurry.

Not only does the equilibrium solubility of limestone (and lime) decrease with increasing chloride concentration, but the rate of limestone dissolution decreases as well. Borgwardt [7] and Rochelle [8] have both shown that the dissolution rate of limestone decreases sharply with increasing chloride concentration when titrated with hydrochloric acid. Borgwardt performed his experiment at a pH of 6.0 and at chloride concentrations up to 10,000 ppm; Rochelle did his at pH 5.0 up to 70,000 ppm. Both experimenters performed tests with NaCl and $MgCl_2$ (as well as $CaCl_2$) and observed that these salts were nearly as effective as $CaCl_2$ in reducing the dissolution rate. Since sodium and magnesium chlorides do not reduce the solubility of limestone by the common ion effect, their influence on the dissolution rate must result from some other effect. Rochelle has modeled the dissolution process and concludes that the suppressed dissolution rate is the result of reduced hydrogen ion diffusivity to the reaction surface of the limestone. Thus, increasing chloride concentration should also reduce $SO_2$ absorption through this negative limestone dissolution effect.

What influences exist to counter these harmful consequences of chlorides? First, two instances where improvement was observed were actually artifacts of the experiment. In the case of both Bechtel [3] and Rader [1], their pilot plant experiments were performed at constant pH. As chloride concentrations increased, the equilibrium pH decreased, resulting in the need to increase the limestone feed rate to maintain the pH set point. Therefore, the increase in $SO_2$ absorption was the result of increasing stoichiometry -- not increasing chlorides. Rader [6] reported that fact after his expanded test program was run at constant stoichiometry.

In a conventional L/L system, the steady-state pH of the recirculated slurry operates at a set point somewhat above the chemical equilibrium pH of the slurry. As a general rule, the difference between these two pH values will decrease as the limestone stoichiometry increases. When chlorides are added to the slurry, the equilibrium pH drops. Therefore, if the stoichiometry is to be maintained constant as chlorides increase, then the set-point pH must also be decreased. Rader [6] has hypothesized that the limestone dissolution rate may increase in this more acid environment and, in so doing, help to moderate these negative influences of chlorides. The extent to which this actually exists has not been experimentally examined in any controlled experiments but is implied to be a factor in Rader's pilot plant results.

Jarvis [9] has presented perhaps the most compelling explanation to indicate why experimenters have at times seen slight improvement or at least little degradation in $SO_2$ absorption at elevated chloride levels. Specifically, he has found that the total sulfite solubility actually increases with increasing calcium chloride concentration up to a point and reaches a maximum around 30,000 ppm $Cl^-$. This means that $SO_2$ absorption can increase with increasing chlorides even if the dissolved alkalinity in the absorber reduces slightly. In effect, the make-per-pass capacity of the slurry increases. Computer models of this complex chemical equilibrium among $SO_{2(g)}$, $CO_{2(g)}$, $CaCl_{2(aq)}$, and $H_2O_{(l)}$ can be shown to support this experimental observation. A B&W-modified form of the Radian chemical equilibrium model suggests that the enhanced sulfite solubility is principally the result of ion pairing between $Ca^{++}$ and $HSO_3^-$ as $CaHSO_3^+$.

## THEORY

$SO_2$ absorption into the absorber slurry is enhanced by chemical reaction with dissolved species. The dissolved species that are thought to participate include:

$$SO_{2(g)} \overset{H_2O}{\rightleftharpoons} SO_{2(aq)} \quad (R2)$$

$$SO_{2(aq)} + CaSO_4^{\circ} + H_2O \rightleftharpoons HSO_3^- + HSO_4^- + Ca^{++} \quad (R3)$$

$$SO_{2(aq)} + SO_4^{=} + H_2O \rightleftharpoons HSO_3^- + HSO_4^- \quad (R4)$$

$$SO_{2(aq)} + CaSO_3^{\circ} + H_2O \rightleftharpoons 2HSO_3^- + Ca^{++} \quad (R5)$$

$$SO_{2(aq)} + CaHCO_3^+ \rightleftharpoons HSO_3^- + Ca^{++} + CO_2 \quad (R6)$$

$$SO_{2(aq)} + HCO_3^- \rightleftharpoons HSO_3^- + CO_2 \quad (R7)$$

$$SO_{2(aq)} + SO_3^{=} + H_2O \rightleftharpoons 2HSO_3^- \quad (R8)$$

Slurry entering the absorber at the spray nozzles will tend to approach equilibrium among the following species: $CO_{2(g)}$, $CaCO_{3(s)}$, $CaSO_3 \cdot 1/2\ H_2O_{(s)}$, $CaSO_4 \cdot 2H_2O_{(s)}$, and $H_2O$/pH = set point. The equilibrium composition can be computed for example, by B&W's modification of the Radian's chemical equilibrium model. However, one uncertainty is what value to assign to the $CO_2$ partial pressure. Values ranging from $3 \times 10^{-4}$ atm to 1.0 atm are possible.

Increasing $CO_2$ partial pressure increases the bicarbonate concentration. This benefits $SO_2$ absorption via Reaction 7. Most investigators assume a value of 0.1 to 1.0 atm. The sum of the molar concentration of these reacting species is often called the "dissolved alkalinity."

A question of fundamental importance to the design of limestone absorption systems is whether within the $SO_2$ absorber the reaction system is limited to homogeneous liquid-phase reactions, such as Reactions 3 through 8. The question reduces to whether sufficient time exists for calcium carbonate and/or calcium sulfite to dissolve within the absorber via:

$$CaCO_{3(s)} \underset{}{\overset{H_2O}{\rightleftharpoons}} Ca^{++} + CO_3^{=} \qquad (R9)$$

$$CaSO_3 \cdot 1/2\ H_2O_{(s)} \overset{H_2O}{\rightleftharpoons} Ca^{++} + SO_3^{=} + 1/2\ H_2O \qquad (R10)$$

TVA [10] has reasoned that Reaction 9 can be a significant contributor to the alkalinity of a limestone system but that Reaction 10 is probably unimportant, except in lime FGD systems.

Alternatively, direct reaction between $H^+$ and limestone has been postulated at the limestone surface to proceed via:

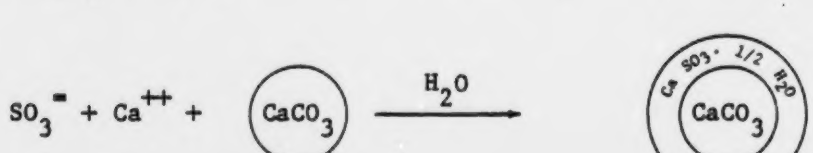
$$H^+ + CaCO_{3(s)} \rightleftharpoons Ca^{++} + HCO_3^- \qquad (R11)$$

While the homogeneous reactions can be assumed to be instantaneous, the heterogeneous reactions (R9 through R11) are finite. Further, the rates of these reactions will depend on the surface area of the solid species. Thus, it follows that participation by Reaction 9, for example, will be benefitted by fine grinding of limestone and by maximizing residence time of slurry within the absorber.

Therefore, one of the major questions addressed in this pilot plant test program was to determine whether harmful effects of chlorides might be alleviated by designing the FGD system to promote the heterogeneous reactions (R9 through R11) in the absorber.

Finally, we should consider the $SO_2$/limestone reaction system for forced oxidation tests. For these tests where oxidation is nearly complete, Reactions 5, 8, and 10 cannot participate. Further, the tendency to blind limestone via the following mechanism is heightened since the system is deficient of sulfite crystals to receive precipitating sulfite.

$$SO_{2(aq)} + H_2O \longrightarrow HSO_3^- + H^+ \longrightarrow SO_3^{=} + 2H^+ \qquad (R12)$$



(R13)

Countering these effects is the fact that the equilibrium and interfacial $SO_2$ vapor pressure are substantially reduced under forced-oxidation operation. This should enhance $SO_2$ absorption. On balance, it seems reasonable to expect that $SO_2$ performance under conditions of forced oxidation may be more sensitive than the natural oxidation tests to the limestone grind size.

## TEST PROGRAM PLAN

A factorialized test plan was devised for this program. The variables selected and the levels to be tested were:

| VARIABLES | | LEVELS | |
|---|---|---|---|
| Mode of Oxidation | | Natural | Forced |
| Limestone Grind: | Fine | 95% through 325 mesh | 95% through 325 mesh |
| | Coarse | 80% through 200 mesh | 80% through 200 mesh |
| Inlet $SO_2$ Concentration | | 2000 ppm, 4000 ppm | 2000 ppm, 4000 ppm |
| L/G | | 45, 90 gal/MCF | 45, 90 gal/MCF |
| Recirculation Tank Residence Time | | 5.6, 11.2 min | 5.6, 11.2 min |
| Liquid Holdup | | 0, 3, and 6 inches | 0 |
| Chloride Concentration | | 0, 15,000, 30,000, 45,000, 60,000 | 15,000, 30,000, 45,000, 60,000 |

The specification for limestone grind was intended to evaluate the extremes of normal commercial practice as were the specifications for L/G and tank residence. The specification for $SO_2$ concentration at the inlet was intended to examine the usual range for eastern bituminous coals. Actually, the specification of 2000 ppm was to be obtained by burning eastern Kentucky coal in Unit 10 at the Shawnee Steam Plant. In fact, during the test program, actual $SO_2$ level varied from about 2200 to 2600 ppm because of variations in factors like sulfur content of the coal, boiler load, excess air, etc.

The three levels of "liquid holdup" expressed as 0, 3, and 6 inches represent the approximate hydraulic head in inches of water of retained slurry in the absorber. Actually, the physical variable was the number of sieve trays in the absorber. Zero holdup represents the spray tower configuration with no tray. The 3-inch holdup represents the use of one sieve tray, and the 6-inch holdup represents the use of two sieve trays.

The five levels of chloride are spread uniformly over the full range that we anticipate might be experienced even under extreme conditions. The zero level really represents the open-loop concentration, which could amount to several hundred ppm.

In addition to the variables selected for study, careful consideration was given to the absorber parameter settings that were to be held invariant. Tower velocity of 10 ft/sec and 15% suspended solids were selected as normal absorber settings. Spray nozzle pressure of 4 psi is somewhat low by FGD standards (10 - 15 psi is more usual). The nozzles used in this program were selected mainly to reduce the wall effect within the absorber.

The most difficult operating parameter to select was for limestone stoichiometry*. A limestone stoichiometry set point of 1.10 (±0.01) was established for most tests. There are distinct difficulties in attempting to operate a pilot plant at such a low stoichiometry. These include:

- $SO_2$ performance may be very sensitive to small variations in stoichiometric ratio.

- Control of stoichiometry is more difficult as the stoichiometric ratio set point is lowered.

Despite these legitimate concerns, our overriding objective was to model current industrial practice in FGD. Most limestone-based FGD systems are designed to operate at low stoichiometries (1.1 to 1.15). Most chloride/FGD studies to date have been performed at relatively high stoichiometry (greater than 1.3). Considering these facts, we decided to specify the stoichiometric ratio at 1.1, with the understanding that if operating the pilot plant became too difficult, the set point would be raised.

## TEST RESULTS

The influence of chlorides on $SO_2$ absorption was analyzed in four parts:

- Natural oxidation tests using finely ground limestone
- Natural oxidation tests using coarsely ground limestone
- Forced oxidation tests using fine limestone
- Forced oxidation tests using coarse limestone

Statistical analysis of 161 tests produced the correlations in Table 1. The number of transfer units ($N_T$) as utilized in these correlations is related to $SO_2$ absorption ($f_{SO_2}$) by:

$$-\ln(1 - f_{SO_2}) \equiv N_T \qquad \text{(E6)}$$

The influence of chlorides on $SO_2$ absorption can be thought of as a negative enhancement in a manner similar to Dankwertz's enhancement factor. Laslo [11] has adapted that procedure by defining a term that we will call the "diminution factor" as follows:

$$\alpha = \frac{N_T \text{ at Cl} = \text{Cl}}{N_T \text{ at Cl} = 0} \qquad \text{(E7)}$$

---

*Limestone stoichiometry (or stoichiometric ratio) refers here to the molar ratio of calcium carbonate added to the FGD system to the moles of sulfur dioxide absorbed by the system. This term is sometimes referred to in the FGD literature as reagent ratio.

## Table 1

## $SO_2$ ABSORPTION CORRELATIONS

### Natural Oxidation Plus Fine Grinding

$$N_T = \left[\frac{S_R - 1.0}{0.1}\right]^{1/3} \Big[- 0.0762 + 0.001496\ (\mathrm{Cl}/1000) - 0.4559 \times 10^{-4}\ (\mathrm{Cl}/1000)^2 + 0.5346\ T_N + 0.02509\ L_f - 0.8835 \times 10^{-4}\ (T_N)(Y_{SO_2}) - 1.365 \times 10^{-6} (L_f)(Y_{SO_2}) - 6.628 \times 10^{-5}\ (\mathrm{Cl}/1000)(L_f)\Big] \qquad (E2)$$

$R = 96.7\%$ $\sigma = 0.09227$

### Natural Oxidation Plus Coarse Grinding

$$N_T = \left[\frac{S_R - 1.0}{0.1}\right]^{1/3} \Big[- 0.1352 - 0.002088\ (\mathrm{Cl}/1000) - 0.7832 \times 10^{-5}\ (\mathrm{Cl}/1000)^2 + 0.2350\ T_N + 0.02938\ L_f - 0.8456 \times 10^{-5}\ (T_N)(Y_{SO_2}) - 0.3669 \times 10^{-5} (L_f)(Y_{SO_2}) + 1.200 \times 10^{-5}\ (\mathrm{Cl}/1000)(L_f)\Big] \qquad (E3)$$

$R = 94.1\%$ $\sigma = 0.0132$

### Forced Oxidation Plus Fine Grinding

$$N_T = \left[\frac{S_R - 1.0}{0.1}\right]^{1/3} \Big[0.1393 + 0.003258\ (\mathrm{Cl}/1000) - 0.5008 \times 10^{-4}\ (\mathrm{Cl}/1000)^2 + 0.02718\ (L_f) - 0.3834 \times 10^{-4}\ (Y_{SO_2}) - 0.3210 \times 10^{-5}\ (L_f)(Y_{SO_2}) - 0.4856 \times 10^{-4}\ (L_f)(\mathrm{Cl}/1000)\Big] \qquad (E4)$$

$R = 98.6\%$ $\sigma = 0.0444$

### Forced Oxidation Plus Coarse Grinding

$$N_T = \left[\frac{S_R - 1.0}{0.1}\right]^{1/3} \Big[- 0.1850 + 0.004229\ (\mathrm{Cl}/1000) - 0.2217 \times 10^{-4}\ (\mathrm{Cl}/1000)^2 + 0.03421\ (L_f) + 0.1434 \times 10^{-4}\ (Y_{SO_2}) - 0.5426 \times 10^{-5}\ (L_f)(Y_{SO_2}) - 1.343 \times 10^{-4}\ (L_f)(\mathrm{Cl}/1000)\Big] \qquad (E5)$$

$R = 98.2\%$ $\sigma = 0.059$

The influence of chlorides was analyzed in this manner because of the linear relationship between the diminution factor and the mass transfer coefficient [11]. To relate the overall system $SO_2$ absorption efficiency as a function of the diminution factor, we simply combine Equations 6 and 7 and rearrange to get:

$$E_{SO_2} = \left[1 - (1 - f^{o}_{SO_2})^{\alpha}\right] (100) \qquad (E8)$$

To illustrate the influence that chlorides may have on $SO_2$ performance, Figure 3 was prepared from Equation 8; two circumstances are illustrated. The curves sloping downward from right to left illustrate the loss in efficiency of scrubber systems designed for 90% and 70% $SO_2$ efficiency, respectively. Conversely, the other two curves illustrate to what efficiency new scrubbers must be designed to perform at these efficiencies if a chloride buildup is anticipated.

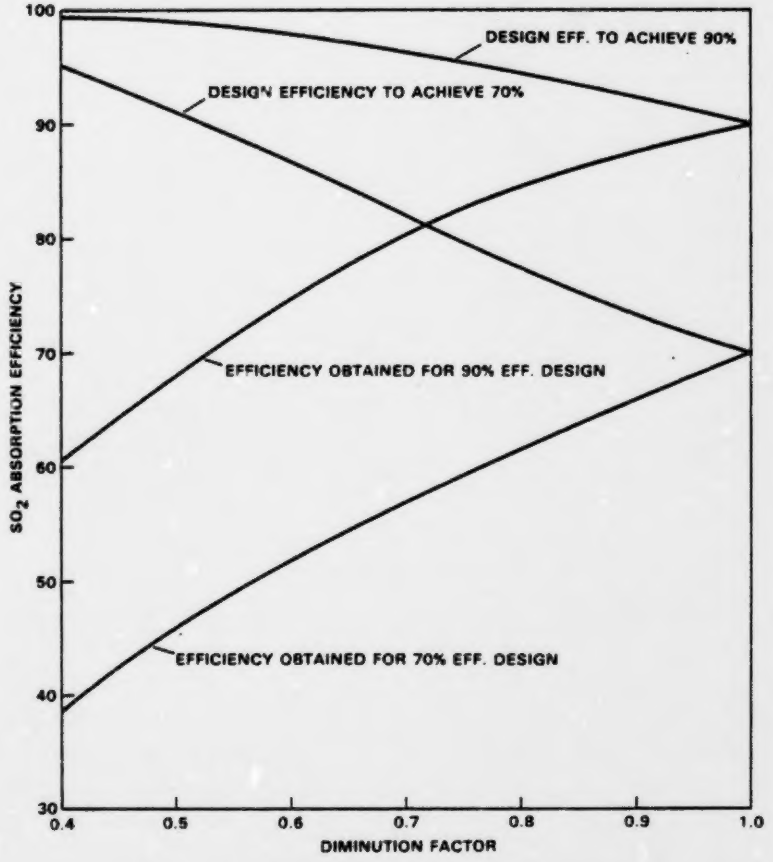


Figure 3. Relationship between diminution factor and $SO_2$ efficiency for high- and low-sulfur coals.

The diminution factors were evaluated from the relationships in Table 1 and are presented in Figure 4. Although the influence of chlorides is significant, the impact was generally less severe than Laslo observed. The observed influence of such variables on $SO_2$ concentration and spray flux* support the general contention that chlorides will affect performance by reducing dissolved alkalinity. Note, for example, that during the natural oxidation tests (Figures 4a through 4f), the diminution factor had its lowest value at the lowest spray flux and highest $SO_2$. At these conditions, the dissolved alkalinity is most rapidly depleted. These figures also reveal the dramatic influence of holdup. The diminution factor is greatly suppressed by including sieve trays, which increase the residence time of the recirculated slurry and, in so doing, permit Reactions 9 through 11 to participate in the absorption process.

The use of trays in the coarse-grind, natural oxidation tests is even more effective. This observation probably results from the fact that with coarsely ground limestone in the spray tower configuration (no trays), the heterogeneous reactions (R9 through R11) participate to a lesser extent than with finely ground limestone. This results in an even faster depletion of alkalinity in the absorber. Then, as holdup is provided by the trays, these reactions became progressively more important.

The influence of chlorides on $SO_2$ absorption during the forced oxidation tests is somewhat more difficult to interpret. During the fine-grind test, $SO_2$ removal enhancement was actually observed. This enhancement could be due to magnesium and sodium impurities, which tend to dissolve some sulfates as $MgSO_4$ and $Na_2SO_4$, thereby increasing the dissolved alkalinity. Since all forced oxidation tests were performed without sieve trays, it is difficult to ascertain to what degree limestone dissolution participates to moderate the depletion of dissolved alkalinity as chlorides increased. However, the more severe effect of chloride on $SO_2$ absorption when using coarsely ground limestone may indicate that Reactions 9 and/or 11 may be significant contributors.

If suppression of the chloride diminution factor with increasing holdup is the result of improved limestone dissolution (as opposed to improved calcium sulfite dissolution), then fine grinding should also contribute significantly. To examine this question, we next define a "limestone grind enhancement factor" by:

$$\phi_1 = \frac{N_T \text{ with fine grind}}{N_T \text{ with coarse grind}} \qquad \text{(E9)}$$

where all other independent variables are constant. The fine-grind enhancement factor is therefore the quotient of Equation 2 divided by Equation 3 for natural oxidation and Equation 4 divided by Equation 5 for forced oxidation. The results of this analysis are shown in Figure 5 and reveal that the influence of fine grinding is most significant for the spray tower arrangement.

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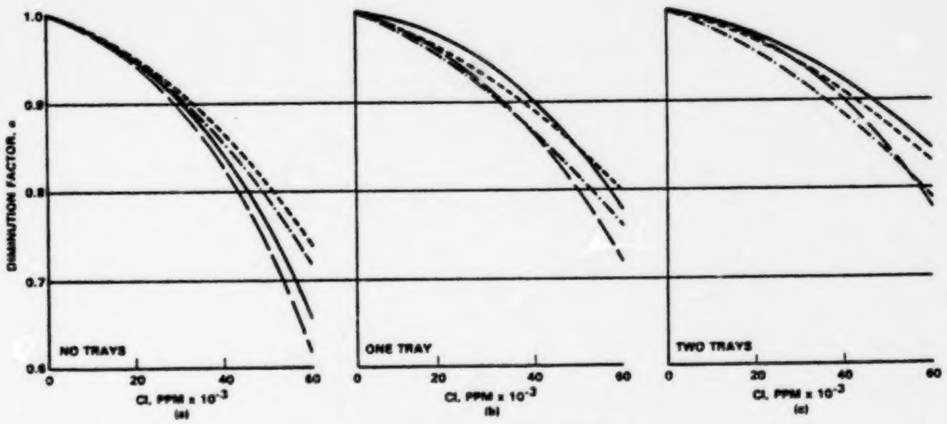
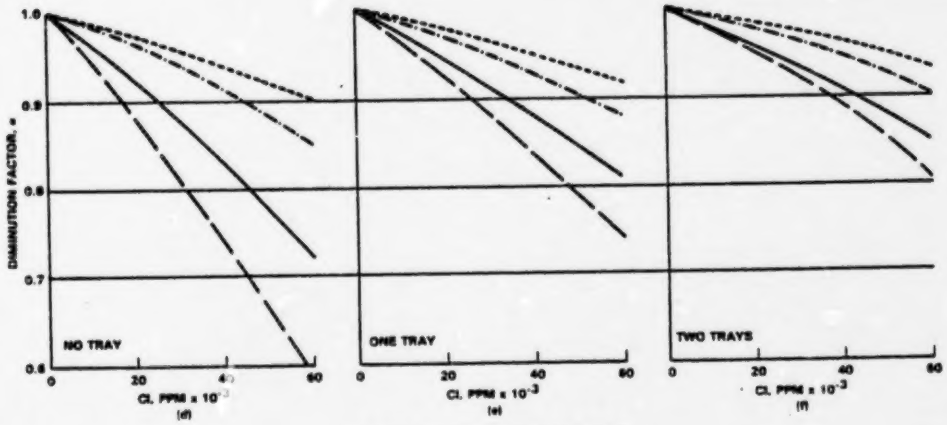
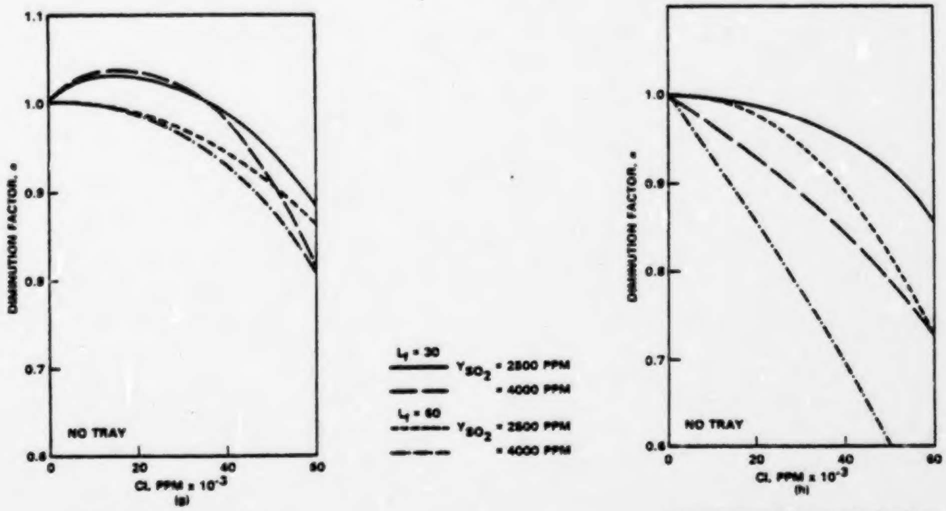
*Spray flux is the normalized slurry recirculation rate in the absorber (gpm/$ft^2$ of absorber flow area).



NATURAL OXIDATION AND FINE GRIND



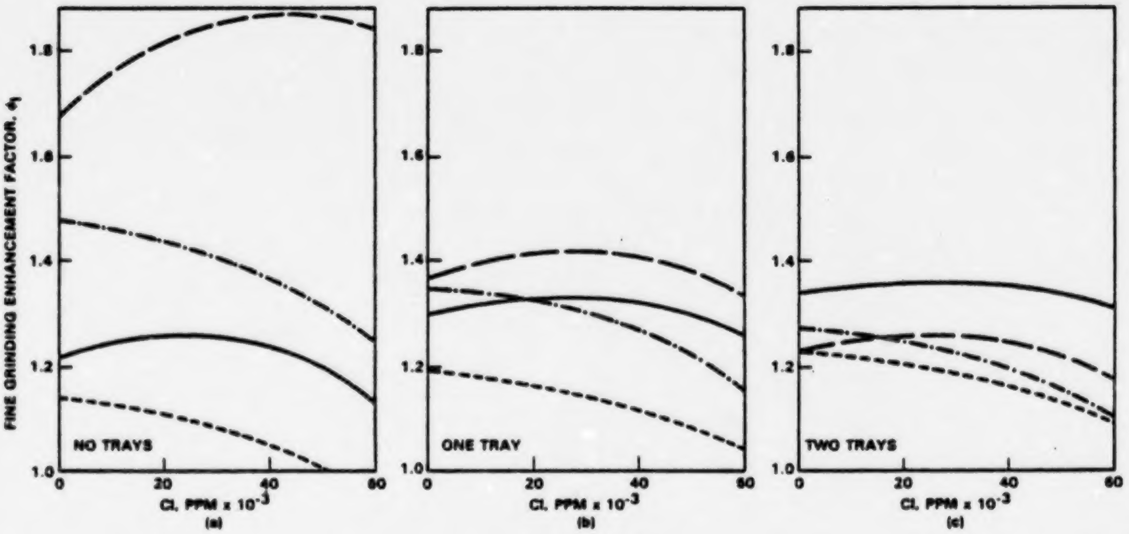
NATURAL OXIDATION AND COARSE GRIND



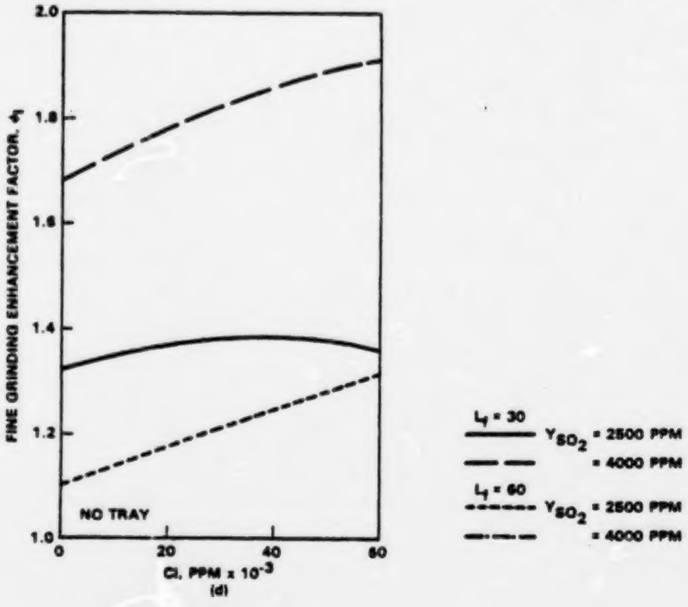
FORCED OXIDATION AND FINE GRIND

FORCED OXIDATION AND COARSE GRIND

Figure 4. Influences of chlorides on $SO_2$ absorption.



NATURAL OXIDATION



FORCED OXIDATION

Figure 5. Fine-grind enhancement of $SO_2$ absorption.

However, the benefit of fine grinding reduces as holdup increases. Taken as a whole, the benefits of fine grinding do not change significantly with chloride concentration. Fine grinding seems to be significantly more beneficial when $SO_2$ concentrations are high (4000 ppm) and spray flux is low. This fact supports the contention that Reaction 9 and/or reaction 11 do participate in the $SO_2$ absorption process.

Next, we examine the influence of forced oxidation on system performance. Recall that forced oxidation offers a trade-off; neither dissolved sulfite nor solid sulfite is present to provide a source of alkalinity. On the other hand, $SO_2$ vapor pressure at the liquid-gas interface is negligible.

To examine the influence of forced oxidation, we again define an enhancement factor, specifically the "forced oxidation enhancement factor," by:

$$\phi_f = \frac{N_T\text{, forced oxidation}}{N_T\text{, natural oxidation}} \tag{E10}$$

The results of this analysis are depicted in Figure 6 for finely ground limestone. We cautiously concluded that for conditions of severely depleted dissolved alkalinity (high $SO_2$ concentration and low-slurry spray rates), the absence of calcium sulfite is significant and produces a reduced level of performance. Conversely, for conditions where dissolved alkalinity is not severely taxed, forced oxidation is beneficial to $SO_2$ removal. These tests also seem to suggest that the benefits of scrubbing with an oxidized slurry improve slightly with increasing chloride concentrations. This further suggests that during natural oxidation tests, calcium sulfite dissolution could be inhibited as the chloride concentration increases. Inhibiting calcium sulfite dissolution by calcium chloride has been observed by Rochelle [12].

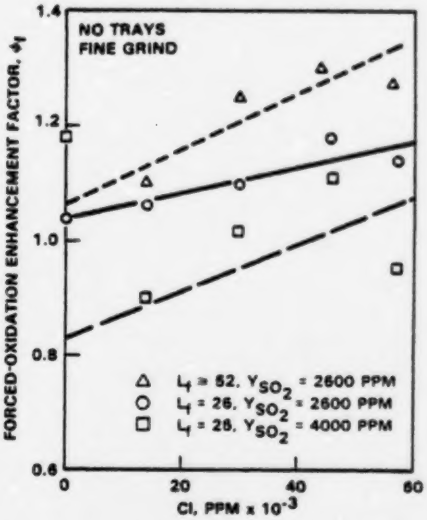


Figure 6. Forced-oxidation enhancement of $SO_2$ absorption with fine limestone.

# SUMMARY AND CONCLUSIONS

The influence of chlorides on FGD performance in limestone processes reduces the rate of $SO_2$ absorption. This diminution results from decreased dissolved alkalinity and from reduced ion diffusivity. The negative impact of chlorides can be suppressed by increasing the spray flux (or L/G), by increasing holdup in the absorber to promote dissolution of calcium sulfite and limestone, and by increasing the limestone fineness. Fine grinding of limestone was a particularly effective way of suppressing the chloride influence during forced oxidation tests.

For example, these analyses suggest that an FGD system (either natural or forced oxidation) designed to achieve 90% $SO_2$ removal in a spray tower employing finely ground limestone (95% passing 325 mesh) and an L/G of 90 gal/MCF should experience an $SO_2$ efficiency loss of only about 2% to 3% at a chloride level of 30,000 ppm.

On commercial FGD absorbers, the influence of spray flux (or L/G) upon the diminution factor may be greater than observed here. With the use of low-pressure nozzles in this test program, the total $SO_2$ mass transfer rate was somewhat less than would be expected for commercial installations. For a given liquid spray flux, therefore, the extent of alkalinity depletion in the pilot program was less than would be expected in a commercial FGD system. Consequently, the influence of chlorides was probably also reduced.

The influences of finely ground limestone on the diminution factor were most noticeable in the spray tower mode (no trays) under conditions of severe alkalinity depletion. The use of trays, high spray flux, and low $SO_2$ concentrations tended to reduce the significance (enhancement) of fine grinding. Commercial FGD processes may be even more responsive to fine grinding than the Shawnee facility, because limestone grinding was done in a dry, closed-loop, ball-mill system. This system appeared to produce a broader particle size distribution than conventional, wet, closed-loop, ball-mill systems. The net effect is that the steady-state limestone surface area of the residual limestone in the recirculating slurry had a lower specific surface area than expected for finely ground limestone (95% passing 325 mesh).

The influence of chlorides in an absorber utilizing a fully oxidized slurry containing finely ground limestone was generally less severe than for the comparable case with a natural oxidized (partially oxidized) slurry. The opposite was true with coarsely ground limestone.

The principal conclusion that can be drawn from this test program is that chlorides do generally inhibit $SO_2$ absorption. However, the severity of this effect can vary widely, depending upon the design and method of operation. The influence of chlorides can be minimized by applying the factors noted here.

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## NOMENCLATURE

Cl = Chloride ion concentration, ppm in liquid phase

$E_{SO_2}$ = $SO_2$ absorber efficiency under the influence of chlorides, %

$f^o_{SO_2}$ = $SO_2$ absorber efficiency in the absence of chlorides, fractional

$f_{SO_2}$ = $SO_2$ absorber efficiency, fractional

$K_{sp1}$ = Solubility product of $CaCO_3$

$K_{sp2}$ = Solubility product of $CaSO_3 \cdot 1/2\ H_2O$

$K_{sp3}$ = Solubility product of $CaSO_4 \cdot 2H_2O$

$L_f$ = Slurry spray flux, gpm/ft$^2$

$N_T$ = Number of transfer units

$S_R$ = Stoichiometric ratio (reagent ratio), moles $CaCO_3$ added/mole $SO_2$ absorbed

$T_N$ = Number of sieve trays

$Y_{SO_2}$ = Inlet $SO_2$ concentration, ppm

( ) = Activity, molarity

$\alpha$ = Diminution factor

$\phi_1$ = Fine-grind enhancement factor

$\phi_f$ = Forced-oxidation enhancement factor

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# EFFECT OF HIGH DISSOLVED SOLIDS ON BENCH-SCALE FGD PERFORMANCE

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## ABSTRACT

To minimize wastewater treatment costs, utilities are evaluating the use of cooling tower blowdown as makeup water for wet limestone FGD systems. If closed loop operation is employed, the dissolved species in the makeup water can be concentrated to significant levels. Additional ions may enter the scrubbing liquor through the absorption of chemical species in the flue gas. An important example is the absorption of HCl produced during the combustion of high chloride coal.

The effect of various high total dissolved solids (TDS) solutions on $SO_2$ removal and other system variables was evaluated in a bench-scale limestone FGD system. Five salts including $CaCl_2$, $MgCl_2$, NaCl, $MgSO_4$, and $Na_2SO_4$ were evaluated under both natural and forced oxidation conditions.

Additional laboratory testing was conducted to isolate specific effects observed in the more complex bench-scale tests. These tests were designed to illustrate the effect of high TDS solutions on chemical equilibria and gas-liquid mass transfer in the absorber.

The results of this investigation show that the performance of the FGD system is determined by the effect of the added salt on: 1) the concentration of dissolved ions in the scrubbing slurry, 2) the solubility of dissolved $SO_2$, 3) mass transfer enhancement through the formation of bisulfite ion pairs with the added cation, 4) sulfate-bisulfate buffering in high sulfate systems, and 5) the mass transfer rate of diffusing species through the liquid film at the gas-liquid interface. The bench-scale test results also compare favorably to the results from similar tests conducted at TVA's Shawnee Test Facility in Paducah, KY. and EPA's pilot facility at Research Triangle Park, NC.

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Prepared for Presentation at EPA/EPRI Symposium on Flue Gas Desulfurization, New Orleans, November 1-4, 1983.

## INTRODUCTION

This paper summarizes selected results from a laboratory study funded by the Electric Power Research Institute to examine the effect of high total dissolved solids (TDS) on $SO_2$ removal in wet limestone FGD systems. Dissolved species such as sodium, magnesium, and chloride can enter the scrubber liquor if process streams such as cooling tower blowdown are used as makeup water to the FGD system. Alternatively, dissolved solids can enter the scrubber liquor through the absorption of soluble species in the flue gas. This situation occurs, for example, when HCl produced during the combustion of high chloride coal is absorbed in the scrubbing liquor along with $SO_2$. HCl reacts with limestone or lime in the scrubber slurry resulting in an accumulation of $CaCl_2$. If closed-loop operation is used, the dissolved solids from either of the above sources can be concentrated to levels which are considerably higher than those presently observed in most systems.

The accumulation of dissolved solids alters scrubber chemistry and can affect $SO_2$ removal, calcium sulfite and sulfate crystal morphology and size, and other process operating characteristics. The remainder of this paper centers on the effect of high TDS solutions on $SO_2$ removal. The data presented here was obtained using Radian's bench-scale FGD system. Five salts including $CaCl_2$, $MgCl_2$, NaCl, $MgSO_4$, and $Na_2SO_4$ were evaluated. Results are presented in three subject areas including:

1) Laboratory batch tests designed to illustrate the effect of high TDS solutions on chemical equilibria and gas-liquid mass transfer;

2) $SO_2$ removal for natural and forced oxidation bench-scale FGD system tests at constant limestone reagent ratio for each of the five salts tested; and

3) Comparisons between the bench-scale FGD system results and the results from similar tests conducted at TVA's Shawnee Test Facility in Paducah, KY. and EPA's pilot facility at Research Triangle Park, NC.

## LABORATORY BATCH TEST RESULTS

A series of laboratory experiments were performed to investigate the effect of each of the tested salts on chemical equilibria and gas-liquid mass transfer:

- The liquid-side and gas-side mass transfer coefficients, $k_\ell a$ and $k_g a$, were determined for the bench-scale bubbler contactor in both a low TDS solution and a concentrated NaCl solution. The purpose of these tests was to determine the effect of the high TDS solution on the physical mass transfer rate of dissolved $SO_2$.

- Experiments were conducted to determine the effect of TDS composition and concentration on the solubilities of dissolved $SO_2$ and total sulfite at constant $SO_2$ partial pressure.

The results of these laboratory tests illustrate several important aspects of the effect of high TDS solutions on $SO_2$ removal. As a package, these results are extremely useful in interpreting the results of the more complex bench-scale FGD system tests presented later in this paper.

## DETERMINATION OF THE BUBBLER SCRUBBER MASS TRANSFER COEFFICIENTS

The local gas-side and liquid-side mass transfer coefficients were determined for the bubbler contactor used in the majority of the bench-scale FGD system tests. The gas-side coefficient, $k_g a$, was measured by once-through scrubbing with a 0.1 N NaOH solution. The liquid-side coefficient, $k_\ell a$, was measured by once-through scrubbing with a 0.5 N HCl solution. In each case, the mass transfer coefficients were measured in a low TDS solution (pure acid or base) and in a concentrated NaCl solution (150,000 ppm $Cl^-$ as NaCl). The purpose of these tests was to determine if the higher density and viscosity of the NaCl solution would result in a change in the scrubber mass transfer characteristics.

With the techniques utilized in this experiment, a change in $k_g a$ would represent a change in the interfacial area available for mass transfer. The experimental results show that $k_g a$ decreased by only about 5 percent with the addition of the concentrated NaCl solution indicating that the increased solution density and viscosity did not have a significant effect on the gas-liquid contacting characteristics of the bubbler absorber. It should be emphasized that this result is specific to the bubbler absorber and may not hold true for all scrubber configurations. In a spray tower, for example, high TDS solutions could affect nozzle performance and result in an increase in droplet size. This could change $k_g a$ significantly by reducing the total surface area available for mass transfer.

In strong acid, the liquid-side mass transfer coefficient, $k_\ell a$, is a function of the rate of surface renewal or turbulence in the liquid film and the diffusion rate of dissolved $SO_2$. The experimental results show that $k_\ell a$ decreased about 50 percent with the addition of the concentrated NaCl. This result indicates that the increased density and viscosity of the NaCl solution has a substantial effect on the turbulence within the liquid film and/or the diffusion rate of dissolved $SO_2$. It is impossible to determine from the experimental results which of these factors is most affected. In any case, the decrease in $k_\ell a$ should result in a substantial decrease in $SO_2$ removal, particularly in cases where liquid-phase alkalinity is low.

## EFFECT OF HIGH TDS SOLUTIONS ON $SO_2$ SOLUBILITY

An additional factor affecting the physical mass transfer of dissolved $SO_2$ ($H_2SO_3$) is the $H_2SO_3$ concentration at the gas-liquid interface.

Since the bulk liquid $H_2SO_3$ concentration in typical FGD slurries is generally very low, the liquid phase $H_2SO_3$ concentration at the gas-liquid interface fixes the concentration driving force for $H_2SO_3$ diffusion.

In conventional mass transfer theory, the gas-phase $SO_2$ concentration and the liquid phase $H_2SO_3$ concentration are in equilibrium at the gas-liquid interface and can be related by an expression similar to Henry's Law. The concentration of dissolved $SO_2$ ($H_2SO_3$) was measured by experiment for a variety of TDS solutions at constant $SO_2$ partial pressure. These solutions consisted of acidified water and acidified solutions containing concentrated NaCl, $MgCl_2$, $CaCl_2$, $MgSO_4$, and $Na_2SO_4$ (about 138,000 ppm $Cl^-$ or $SO_4^=$). The experimental results show that the equilibrium dissolved $SO_2$ concentration for each of the concentrated salt solutions is about 25 percent (on a weight basis) below that of the acidified water alone. This "salting out" effect, together with the effect of increased viscosity on the liquid-side mass transfer coefficient, suggests that the physical mass transfer rate of $SO_2$ should decrease significantly with increasing ionic strength.

## EFFECT OF HIGH TDS SOLUTIONS ON TOTAL SULFITE SOLUBILITY

Thus far, the discussion of the effect of high TDS solutions has been limited to mass transport by physical absorption and diffusion. The other component of $SO_2$ mass transport in FGD systems is $SO_2$ mass transfer enhancement by chemical reaction. Species which are alkaline with respect to $H_2SO_3$ react with $H_2SO_3$ to form $HSO_3^-$. This reduces the $H_2SO_3$ concentration in the liquid film and increases the driving force for $H_2SO_3$ diffusion. Reactions which remove $HSO_3^-$ from solution also enhance $SO_2$ removal by allowing additional $H_2SO_3$ to dissociate via the hydrolysis reaction:

$$SO_2 + H_2O \rightleftarrows H^+ + HSO_3^- \qquad (1)$$

In low TDS solutions, the important alkaline species include $SO_3^=$ and $HCO_3^-$ which can be present initially in the liquid phase or result from the dissolution of calcium sulfite and limestone. In high TDS solutions, however, additional reactions can occur which enhance $SO_2$ removal. The most important of these reactions include the formation of ion pairs involving $HSO_3^-$ and sulfate-bisulfate buffering in high sulfate solutions. High ionic strength solutions also affect $SO_2$ removal enhancement by changing the activity coefficients of other dissolved species.

The alkalinity provided by ion pairing and sulfate-bisulfate buffering was measured for each of the five salts studied during this program by equilibrating the pure salt solutions with an $N_2$-$SO_2$ gas stream at fixed $SO_2$ partial pressure. The $SO_2$ absorbed into solution exists as $H_2SO_3$, $HSO_3^-$, $SO_3^=$, and ion pairs containing $HSO_3^-$ and $SO_3^=$. The observed total sulfite concentration is a measure of the ability of the salt solution to enhance $SO_2$ removal through the hydrolysis reaction, the formation of ion pairs, and sulfate-bisulfate buffering in high sulfate solutions. In practice, the alkalinity of the scrubber slurry is augmented by $SO_3^{=}$ and $HCO_3^-$ initially present in solution and dissolution of limestone and calcium sulfite.

The experimental results illustrated in Figure 1 show the total sulfite concentration absorbed into the salt solution versus the chloride or sulfate concentration of the salt tested. Note that the measured total sulfite concentrations have been divided by the $SO_2$ partial pressure (about 1.38 mm Hg ave.) for the purpose of normalizing for small variations in the gas phase $SO_2$ concentration. The results show that the total dissolved sulfite concentration is a strong function of the composition and concentration of the salt tested. For the chlorides, an increase in total dissolved sulfite is seen up to about 30,000 ppm $Cl^-$. The amount of dissolved sulfite falls off at higher chloride concentrations. The largest degree of enhancement at the 30,000 ppm $Cl^-$ level is observed with $CaCl_2$. The least enhancement occurs with NaCl. Total dissolved sulfite concentrations in the sulfate solutions were considerably higher than those seen in the chloride solutions due to sulfate-bisulfate buffering.

The effect of TDS composition and concentration on total sulfite solubility plays a significant role in determining the $SO_2$ removal level in FGD systems. These effects are quite apparent in the bench-scale FGD system results which follow.

## BENCH-SCALE FGD SYSTEM TEST RESULTS WITH HIGH TDS SOLUTIONS

A total of 36 bench-scale tests were performed to evaluate the effect of TDS composition and concentration on $SO_2$ removal. The core of this test series consisted of 10 runs in which the effect of each of the five salts tested was evaluated under both forced and natural oxidation conditions. These runs were performed at a constant limestone loading of about 10 g $CaCO_3$/l which is approximately equivalent to a limestone reagent ratio of 1.10 at 15 wt. percent solids. The limestone used in these tests was high calcite Edwards limestone (100% through 200 mesh, 95% through 325 mesh).

A schematic diagram of Radian's bench-scale FGD system is given in Figure 2. Synthetic flue gas containing $N_2$, $O_2$, $CO_2$, and $SO_2$ was saturated with $H_2O$ to about 40°C and fed to the absorber. For most tests, the flue gas composition (dry basis) was 77% $N_2$, 7% $O_2$, 16% $CO_2$, and 2000 ppm $SO_2$.

The bench-scale scrubber process flow diagram is essentially the same as that for a full-scale FGD system. Slurry from the hold tank is fed to the absorber where it contacts the flue gas. The scrubber effluent is recycled back to the hold tank. Closed-loop operation is achieved by sending a portion of the hold tank slurry to an in-line filter. Clear filtrate is then returned to the hold tank. The temperature of the hold tank was maintained at 50°C by recycling part of the slurry through coils in a heated water bath.

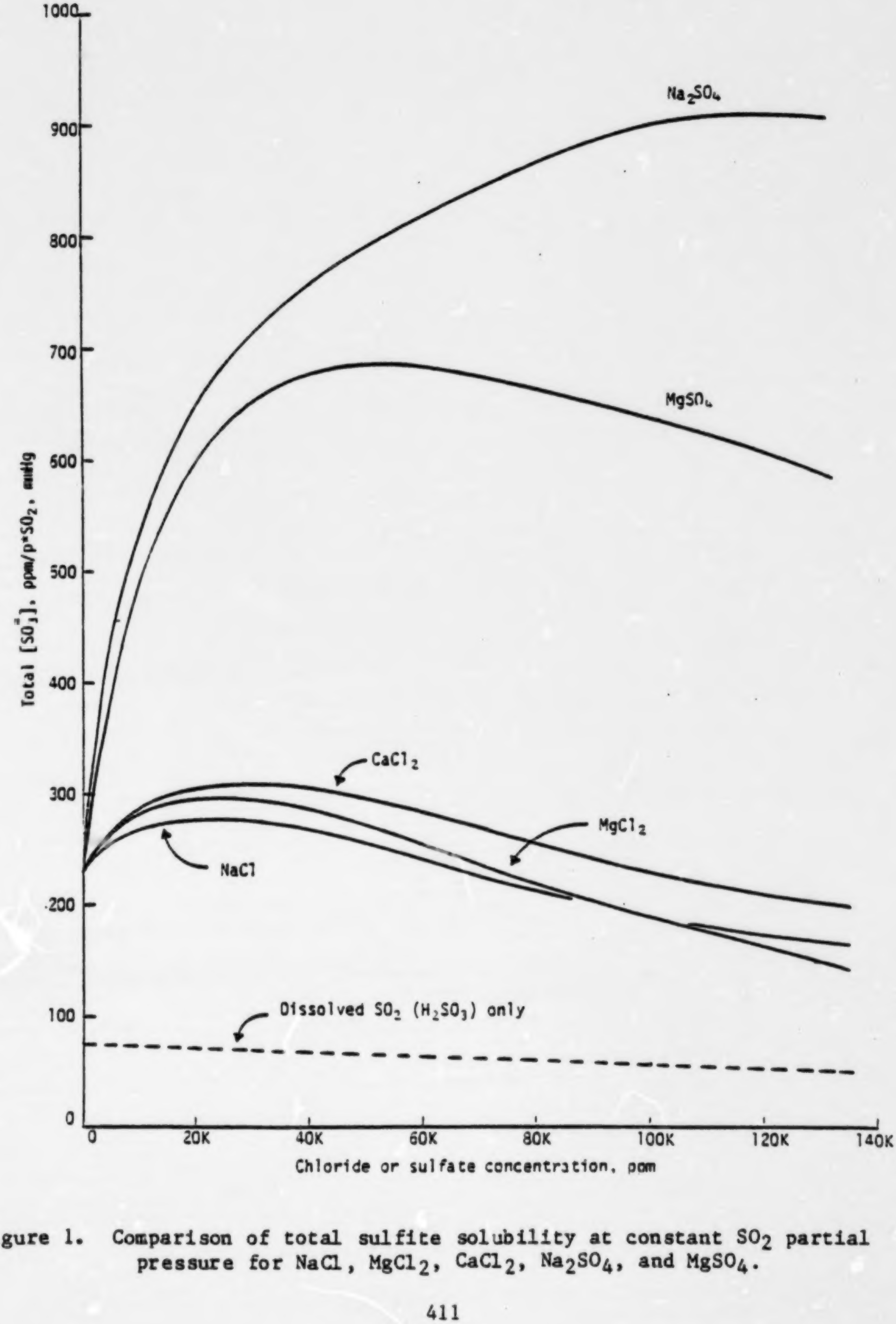


Figure 1. Comparison of total sulfite solubility at constant $SO_2$ partial pressure for NaCl, $MgCl_2$, $CaCl_2$, $Na_2SO_4$, and $MgSO_4$.

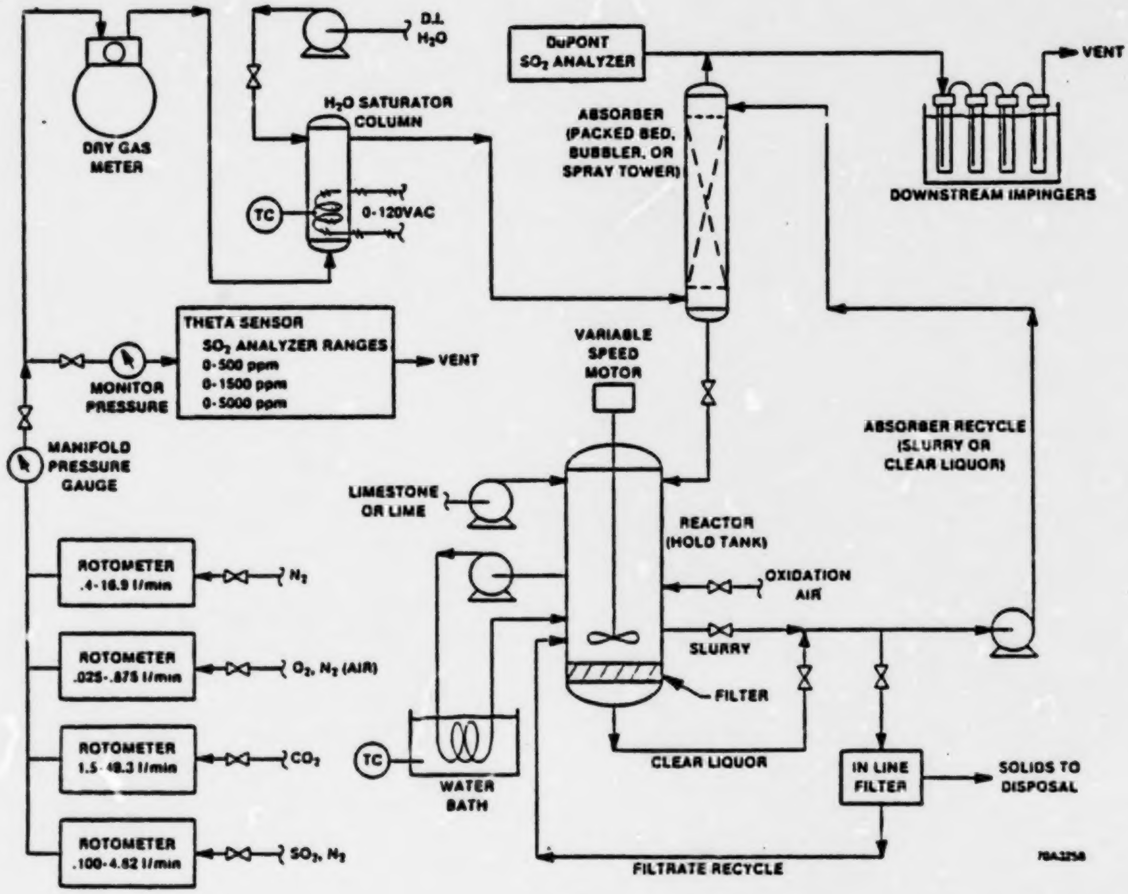


Figure 2. Schematic diagram of the bench-scale FGD system.

A bubbler contactor was used for most of the bench-scale tests conducted in this program. The bubbler was designed such that L/G, gas-liquid contact time, and the residence time of slurry within the contactor could be varied independently. The flow characteristics within the scrubber are best described as plug flow with respect to the gas phase and back-mixed with respect to the liquid phase. In this configuration, the bench-scale scrubber is intended to simulate the $SO_2$ removal characteristics of a tray tower with a single tray.

The $SO_2$ removal results for the natural and forced oxidation runs are shown in Figures 3 and 4, respectively. For the natural oxidation runs in Figure 3, the initial and final total sulfite concentrations for each test are also listed.

For NaCl, a slight enhancement in $SO_2$ removal is seen for both forced and natural oxidation at chloride levels of about 15,000-20,000 ppm. $SO_2$ removal decreases substantially, however, at higher chloride levels. The initial enhancement in $SO_2$ removal is the result of the increase in total sulfite solubility as shown in Figure 1. The subsequent decrease in $SO_2$ removal is the result of at least three factors:

1) A decrease in total sulfite solubility above the 20,000 ppm $Cl^-$ level (see Figure 1),

2) A decrease in the liquid-side mass transfer coefficient with increasing chloride concentration, and

3) A decrease in dissolved $SO_2$ ($H_2SO_3$) solubility with increasing ionic strength.

Note that the sulfite concentration has little effect on the change in $SO_2$ removal with NaCl since the low and high chloride level sulfite concentrations are nearly the same for both the natural and forced oxidation runs.

Enhancement in $SO_2$ removal is also observed for $MgCl_2$ at around 25,000 ppm $Cl^-$ for both the natural and forced oxidation runs. The level of enhancement is somewhat higher than that seen for NaCl. This result is expected based on the total sulfite solubility results in Figure 1. At chloride levels above 25,000 ppm $Cl^-$, $SO_2$ removal decreases as a result of the same factors causing decreased $SO_2$ removal with NaCl. The decrease in $SO_2$ removal for the natural oxidation run with $MgCl_2$ was not as severe as with NaCl, however, due to an increase in liquid phase sulfite at high $MgCl_2$ concentrations.

Based on the total sulfite solubility results in Figure 1, considerable enhancement in $SO_2$ removal should be observed with $CaCl_2$. In fact, the level of enhancement should be the highest of the three chloride salts

FIGURE 3. COMPARISON OF THE EFFECT OF NaCl, $MgCl_2$, $CaCl_2$, $Na_2SO_4$, AND $MgSO_4$ ON $SO_2$ REMOVAL FOR NATUARAL OXIDATION AT CONSTANT LIMESTONE REAGENT RATIO.

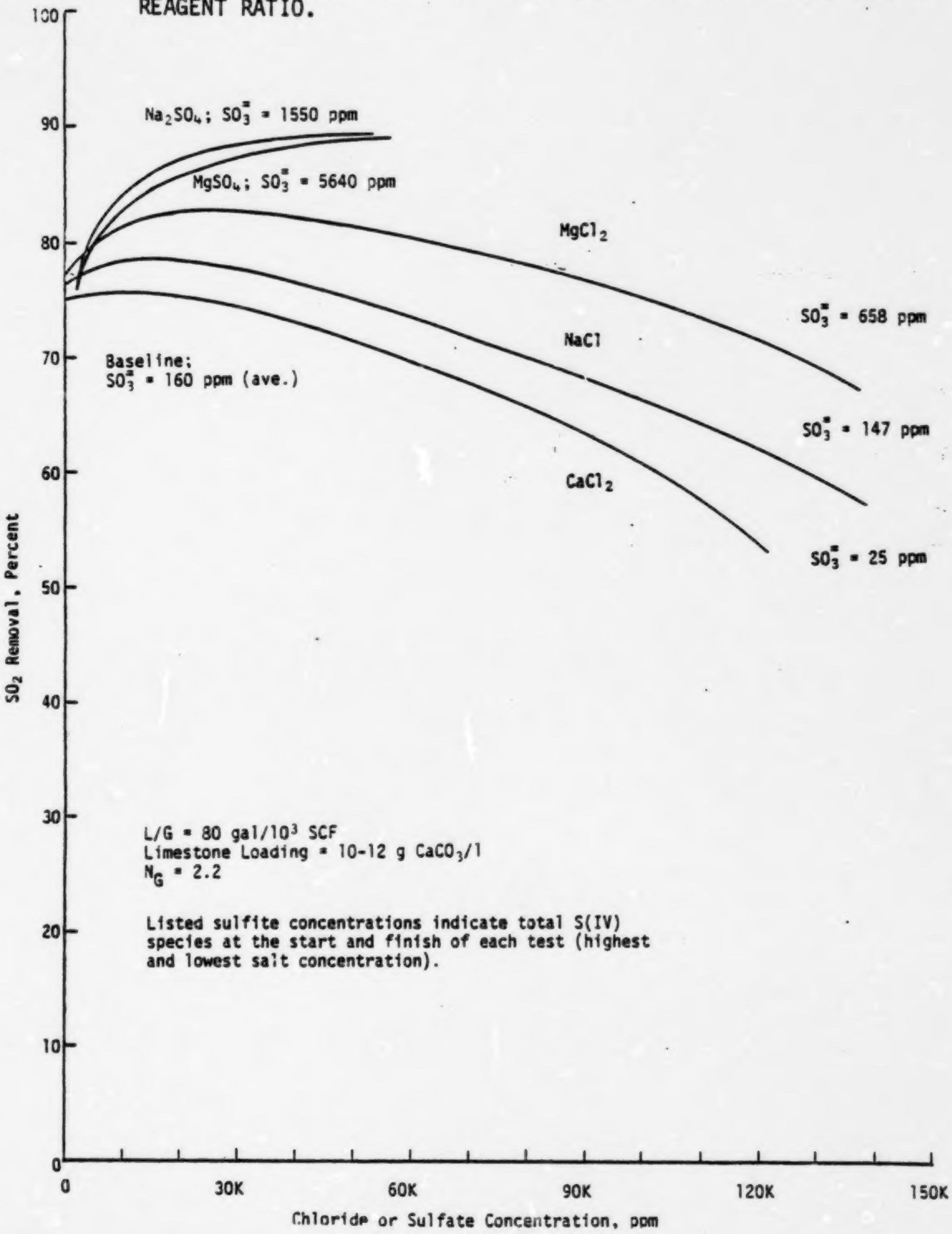
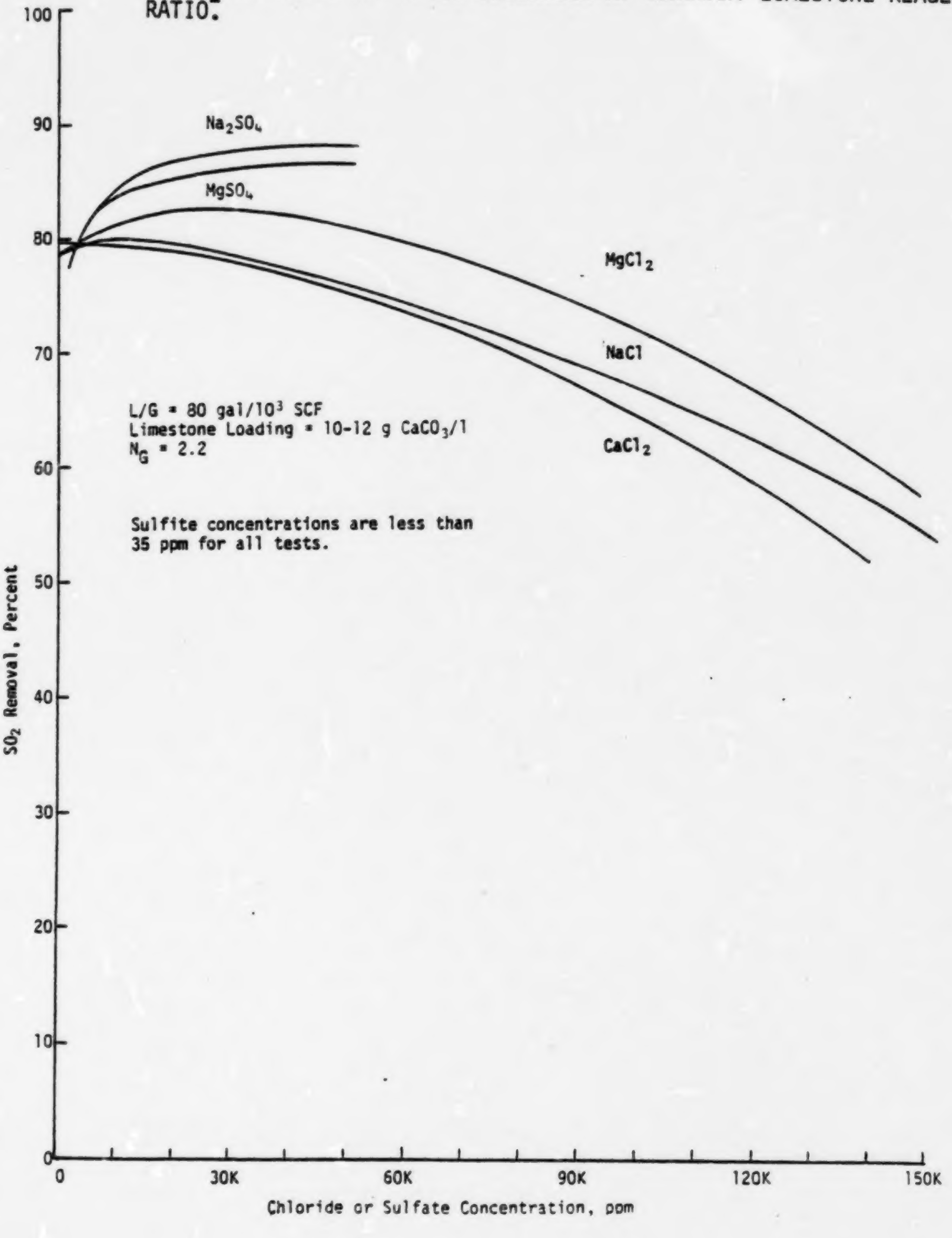


FIGURE 4. COMPARISON OF THE EFFECT OF NaCl, $MgCl_2$, $CaCl_2$, $NaSO_4$, AND $MgSO_4$ ON $SO_2$ REMOVAL FOR FORCED OXIDATION AT CONSTANT LIMESTONE REAGENT RATIO.



tested. However, the data in Figures 3 and 4 show that no enhancement was observed with $CaCl_2$ at chloride levels around 25,000 ppm. With $CaCl_2$, the enhancement expected from the increase in total sulfite solubility is offset by a decrease in the feed liquor concentrations of total $SO_3^=$ and $CO_3^=$. As shown in Table 1, a decrease in total $SO_3^=$ and $CO_3^=$ occurs with increasing $Ca^{++}$ due to the common ion effect. The net result of these two competing factors is little, if any, effect on $SO_2$ removal for the bench-scale tests at chloride levels up to 20,000 ppm.

At high chloride concentrations, $SO_2$ removal for natural oxidation with $CaCl_2$ is considerably below that for either $MgCl_2$ or NaCl. As indicated in Figure 3, this is probably caused by the differences in the $SO_3^=$ concentrations in solution. In forced oxidation, however, the $SO_3^=$ concentration is low for all three chloride salts and the high chloride $SO_2$ removals are much closer together.

One other consideration involving $CaCl_2$ should be mentioned. In operating FGD systems, high $CaCl_2$ concentrations will most likely occur as a result of the combustion of coal containing chlorine. The combustion product, HCl, will be absorbed in the scrubber along wtih $SO_2$ and will consume a portion of the alkalinity in the scrubbing liquor. The effect of the absorption of HCl on $SO_2$ removal was not considered in the bench-scale study.

The natural oxidation results in Figure 3 for $MgSO_4$ and $Na_2SO_4$ show that the $SO_2$ removals increased significantly from the baseline level and approached the maximum possible $SO_2$ removal level for the contactor. This result is not surprising in view of the high sulfite concentrations in the scrubbing liquor. What is surprising, however, is that $SO_2$ removals in the forced oxidation tests in Figure 4 were only slightly below the corresponding natural oxidation tests even though the liquid phase sulfite concentrations were very low. The high $SO_2$ removals for the forced oxidation tests with $SO_4^=$ are the result of the large increase in total sulfite solubility (Figure 1) caused by the combination of ion pair formation and sulfate-bisulfate buffering.

## COMPARISON OF BENCH-SCALE, SHAWNEE, AND RTP HIGH CHLORIDE TEST RESULTS

One of the benefits of bench-scale testing is that it allows the evaluation of important process variables at costs which are well below those of similar tests on larger units. In addition, the flexibility inherent to bench-scale systems along with better control over process variables allows tests to be conducted which are impossible at full-scale. To be of value, however, the bench-scale tests must adequately predict the results seen with larger units.

The results of three test programs in which the effect of $CaCl_2$ on $SO_2$ removal was evaluated are compared in the following paragraphs. These programs include the bench-scale FGD system tests described in this paper, a high $CaCl_2$ test program conducted by Babcock and Wilcox at TVA's Shawnee

TABLE 1. EFFECT OF $CaCl_2$ ON THE CONCENTRATION OF DISSOLVED SOLIDS

| Bench-scale Run No. | $CaCl_2$ Conc., ppm $Cl^-$ | Total $SO_3^=$, ppm | $SO_4^=$, ppm | Total $CO_3^=$, ppm |
|---|---|---|---|---|
| TDS-13 | 13 | 167 | 1938 | 184 |
| Natural | 1,780 | 142 | — | — |
| Oxidation | 4,330 | 101 | — | — |
| | 8,460 | 86 | — | — |
| | 16,600 | 80 | — | — |
| | 32,800 | 62 | — | — |
| | 63,000 | 46 | — | — |
| | 89,400 | 40 | — | — |
| | 121,000 | 25 | 102 | 76 |
| TDS-14 | 19 | 14 | 1923 | 108 |
| Forced | 1,700 | 6 | — | 76 |
| Oxidation | 8,850 | — | — | 89 |
| | 16,500 | 4 | — | — |
| | 31,200 | — | — | 59 |
| | 66,700 | — | — | — |
| | 104,000 | — | — | — |
| | 140,000 | 3.5 | 63 | 41 |

prototype facility, and high TDS testing conducted by Peabody Process Systems at EPA's pilot facility at Research Triangle Park (RTP). The effect of $CaCl_2$ on $SO_2$ removal is given in Table 2 for each of the three test programs. Two types of comparisons are presented including:

1) The effect on $SO_2$ removal of an increase in $CaCl_2$ from 0 to 60,000 ppm $Cl^-$ for both forced and natural oxidation, and

2) The difference in $SO_2$ removal between forced and natural oxidation at the 0 and 60,000 ppm $Cl^-$ levels.

The most striking result shown in Table 2 is the dramatic decrease in $SO_2$ removal in the RTP natural oxidation test. In this test, a decrease of 26 percent $SO_2$ removal was observed which is more than twice the decrease seen in either the bench-scale or Shawnee test results. This result is also evident in the comparison of the difference in $SO_2$ removal between forced and natural oxidation. All three test programs show that $SO_2$ removal with forced oxidation is above that for natural oxidation. However, the difference of 18 percent $SO_2$ removal in the RTP tests is greater than four times that seen in either the bench-scale or Shawnee tests. This occurred despite the fact that the limestone reagent ratio in the natural oxidation tests (1.35) was well above that used in the forced oxidation tests (1.20).

From the available data, it would appear that excessive limestone blinding had occurred in the RTP tests. Several additional bench-scale tests were performed to investigate the cause of the rapid decrease in natural oxidation $SO_2$ removal at RTP. These tests included:

- Operation with limestone from the RTP facility,
- A determination of the effect of hold tank $CO_2$ partial pressure (at 80,000 ppm $Cl^-$),
- Simulation of potential limestone blinding in the scrubber effluent line, and
- A determination of the effect of calcium sulfite dissolution in the scrubber.

Although these tests increased our understanding of the effect of $CaCl_2$ on FGD system operation, none of the test results indentified the cause of the drastic decrease in $SO_2$ removal in the natural oxidation RTP tests. Calcium sulfite precipitation within the scrubber was observed at higher chloride levels and limestone reagent ratios. However, this did not result in limestone blinding.

The data in Table 2 show reasonable agreement between the bench-scale and Shawnee results. For forced oxidation, the bench-scale and Shawnee results show decreases of 7 and 8 percent $SO_2$ removal, respectively, at the 60,000 ppm $Cl^-$ level. For natural oxidation, the Shawnee results show a

TABLE 2. COMPARISON OF $SO_2$ REMOVAL RESULTS WITH $CaCl_2$ FOR THE BENCH-SCALE, SHAWNEE, AND RTP TEST PROGRAMS*

| | Decrease in % $SO_2$ Removal for an Increase in $CaCl_2$ from 0 to 60,000 ppm $Cl^-$ | | Difference between Forced Oxidation and Natural Oxidation % $SO_2$ Removal** | |
|---|---|---|---|---|
| | Natural Oxidation | Forced Oxidation | 0 ppm $Cl^-$ | 60,000 ppm $Cl^-$ |
| Radian Bench-scale Tests*** | 7 | 7 | 5 | 4 |
| Shawnee Tests**** | 11 | 8 | 1 | 4 |
| RTP Tests***** | 26 | 9 | 2 | 18 |

* All results are for constant limestone reagent ratio tests.

** Forced oxidation $SO_2$ removals were higher than those for natural oxidation in all cases.

*** Tests performed with a bubbler contactor at a limestone loading of 10 g $CaCO_3$/l which is approximately equivalent to a limestone reagent ratio of 1.10 at 15 wt.% solids.

**** Test results generated from Radian's regression model of the experimental data. $SO_2$ removals estimated at the following run conditions: inlet $SO_2$ = 2500 ppm, L/G = 80 gal/$10^3$ ACFM, one gas-liquid contacting tray, fine grid limestone, and a limestone loading of 10 g $CaCO_3$/l (limestone reagent ratio = 1.10).

***** Tests performed in a three-stage turbulent contact absorber. Limestone reagent ratios were 1.35 for natural oxidation and 1.20 for forced oxidation (1).

slightly greater decrease; 11 percent versus 7 percent for the bench-scale tests. The most likely reason for this difference can be seen by comparing the liquid phase concentrations of $Mg^{++}$ and $SO_3^{=}$ typically seen at very low chloride levels:

| | Bench-Scale | Shawnee |
|---|---|---|
| $Mg^{++}$, ppm | 50-60 | 200-250 |
| $SO_3^{=}$, ppm | 150-160 | 600-650 |

The above data show that the Shawnee scrubber liquor typically had higher $MgSO_3$ concentrations than were used in the relatively "clean" bench-scale scrubbing liquor. That is, a slight amount of magnesium enhancement of $SO_2$ removal was present in the Shawnee tests. Therefore, the initial (low chloride) liquid phase alkalinity in the Shawnee liquor was somewhat higher than that of the bench-scale tests. With the addition of $CaCl_2$, however, $MgSO_3$ in solution is quickly converted to $MgCl_2$ through the following reaction:

$$MgSO_3(aq) + CaCl_2(aq) \rightleftarrows CaSO_3(s)\downarrow + MgCl_2(aq) \quad (2)$$

At high $CaCl_2$ levels, the liquid phase concentrations (and liquid phase alkalinity) of the two scrubbing liquors are nearly identical. In both cases, the $SO_3^{=}$ concentrations are very low. Therefore, over the range of 0 to 60,000 ppm $Cl^-$, the net decrease in liquid phase alkalinity is somewhat greater for the Shawnee liquor than for the bench-scale liquor. The result is a slightly greater decrease in $SO_2$ removal for the Shawnee natural oxidation tests.

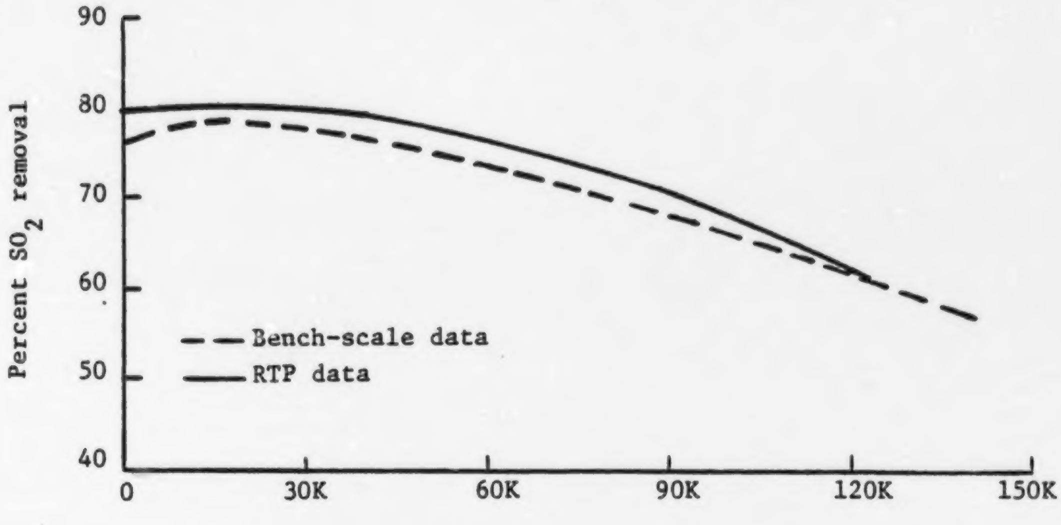
Data have been obtained at the RTP pilot facility on the effect of NaCl and $MgCl_2$ on $SO_2$ removal(2). These data are compared to the bench-scale results for both forced and natural oxidation in Figures 5 through 8. Operating conditions for these tests are summarized below.

| | Radian Tests | RTP Tests |
|---|---|---|
| Inlet $SO_2$, ppm | 2000 | 2500 |
| L/G, gal/$10^3$ cfm | 80 | 60 |
| Contactor | Bubbler (single tray) | TCA |
| Limestone reagent ratio | Fixed at 10g $CaCO_3$/l | 1.1-1.2 |

The results in Figures 5 through 8 show reasonably good agreement between the bench-scale and RTP data.

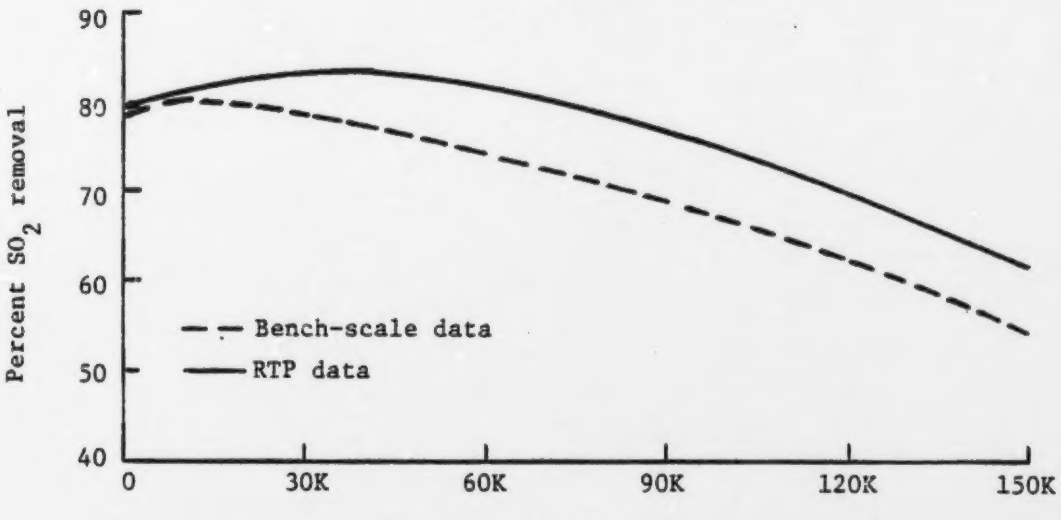
## CONCLUSIONS

1) Chloride affects $SO_2$ removal in wet limestone FGD systems through at least four mechanisms. First, the concentrations of important dissolved



Chloride concentration, ppm

Figure 5. Comparison of bench-scale and RTP data for the effect of NaCl on natural oxidation $SO_2$ removal.



Chloride concentration, ppm

Figure 6. Comparison of bench-scale and RTP data for the effect of NaCl on forced oxidation $SO_2$ removal.

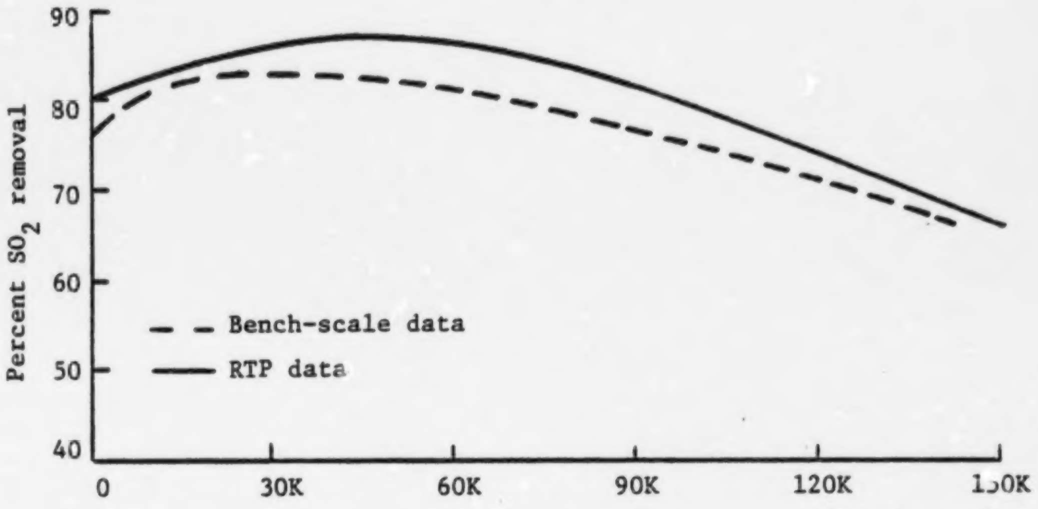


Figure 7. Comparison of bench-scale and RTP data for the effect of $MgCl_2$ on natural oxidation $SO_2$ removal

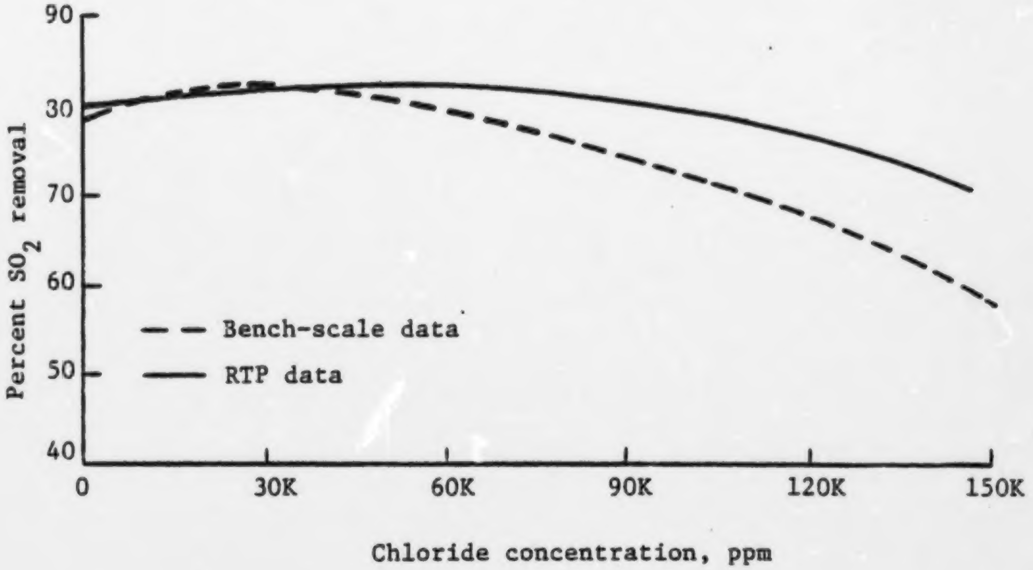


Figure 8. Comparison of bench-scale and RTP data for the effect of $MgCl_2$ on forced oxidation $SO_2$ removal.

species can be affected, depending on which chloride salt is present. In the case of $CaCl_2$, the concentrations of $SO_3^{=}$, $SO_4^{=}$, and $CO_3^{=}$ are reduced due to the common ion effect. Second, the physical solubility of $SO_2$ decreases with increasing ionic strength. This reduces the dissolved $SO_2$ concentration at the gas-liquid interface and decreases the driving force for diffusion of dissolved $SO_2$ through the liquid film. Third, the total sulfite solubility of the salt solution is increased through ion pairing involving bisulfite and the salt cation. For the chlorides, a maximum in the total sulfite solubility is seen around the 30,000 ppm $Cl^-$ level. Finally, mass transfer rates through the liquid film are decreased due to a reduction in the diffusion rates of dissolved species and/or the turbulence in the liquid film.

2) $SO_2$ removal is enhanced in both natural and forced oxidation systems with the addition of sodium or magnesium sulfate salts. In the natural oxidation case, improved $SO_2$ removal can be attributed to increased alkalinity in the form of liquid phase sulfite. $SO_2$ removal under forced oxidation conditions approaches that with natural oxidation. In forced oxidation, the enhancement in $SO_2$ removal with increasing sulfate can be attributed to a substantial increase in total sulfite solubility at the gas-liquid interface through sulfate-bisulfate buffering and the formation of bisulfite ion pairs.

3) Bench-scale tests can be used to predict the effects of high TDS solutions on the operating characteristics of larger FGD units. Bench-scale test results compare favorably to pilot-scale test results from Shawnee for the effect of $CaCl_2$ on $SO_2$ removal. The bench-scale results with $CaCl_2$ also compare favorably with pilot-scale tests at RTP for forced oxidation. However, the drastic decrease in $SO_2$ removal with $CaCl_2$ for natural oxidation at RTP cannot be explained on the basis of either the bench-scale results or the Shawnee results. Good agreement between the bench-scale and RTP results is also seen in natural and forced oxidation tests with $MgCl_2$ and NaCl.

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# Pilot Plant Tests on the Effects of Dissolved Salts on Lime/Limestone FGD Chemistry

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## ABSTRACT

This paper presents an overview of pilot plant testing from September 1981 through June 1983 of the effects of dissolved salts on a lime or limestone flue gas desulfurization (FGD) system at the Environmental Protection Agency's Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina. Tests were conducted using a three-stage turbulent contact absorber (TCA) with a typical gas flow rate (G) of 465 $m^3$/hr (0.1 MW) and absorbing slurry chloride ion ($Cl^-$) concentrations ranging from 160 to 180,000 ppm.

The FGD processes investigated include conventional lime/limestone, magnesia enhanced limestone, and limestone with two-tank forced oxidation. Data indicate that the effects of $Cl^-$ on the performance of the absorber are a function of the cations associated with $Cl^-$ and scrubber operating conditions. The accumulation of calcium chloride caused decreased system pH and $SO_2$ removal efficiency, occasional decreases of slurry settling rate, and increased gypsum scaling potential. When magnesium was the cation, the increase of $Cl^-$ concentration improved $SO_2$ removal efficiency at $Cl^-$ concentrations below 40,000 ppm. No significant effects were observed using sodium chloride at $Cl^-$ concentrations less than 50,000 ppm. However, when $Cl^-$ concentrations were greater than 70,000 ppm, $SO_2$ removal efficiency and system pH declined with the accumulation of either magnesium or sodium chloride. Significant decreases in $SO_2$ removal efficiency were also observed when lime was used in the natural oxidation mode with high inlet $SO_2$ concentrations. Calcium chloride had minor effects on the performance of a DBA enhanced limestone scrubber. Most gypsum specifications required for wallboard manufacturing were met by washing cake using a pilot belt filter.

## ACKNOWLEDGEMENTS

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Coauthor Mobley was the EPA project officer.

## INTRODUCTION

High chloride ion ($Cl^-$) concentrations in the scrubbing liquor are possible with tightly closed water loops in flue gas desulfurization (FGD) systems. If closed-loop operation is assumed (i.e., the only water leaving the FGD system is through evaporation and filter cake moisture), material balance calculations, for high chloride coals, indicate total dissolved solids (TDS, usually the combination of calcium, magnesium, and sodium salts) can accumulate to levels exceeding 50,000 ppm* (1,2). Forced oxidation intensifies the TDS accumulation through improved cake dewatering, and dissolved solids can reach worst case levels in excess of 150,000 ppm (1,2). The origin of the chlorides can be from the coal, as HCl in the flue gas is absorbed, or from chlorides in the makeup water. The latter is especially important if cooling tower blowdown (CTB) is utilized for makeup water. In order to evaluate the effects of $Cl^-$ on FGD system performance, a test program was developed to conduct pilot plant tests under simulated high $Cl^-$ conditions.

This paper presents an overview of a pilot plant test program under the sponsorship of Peabody Process Systems, Inc., and the U.S. Environmental Protection Agency's (EPA) Industrial Environmental Research Laboratory (IERL-RTP) to test the $Cl^-$ effects on wet FGD system performance covering the period from September 1981 through June 1983. For a thorough coverage of the test work, theory, and results, refer to the final report (3). The test facility is located at Research Triangle Park, North Carolina. Acurex Corporation is the major contractor and facility operator.

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* One ppm is equivalent to one mg/l.

## TEST FACILITIES

Two process configurations, natural and forced oxidation, shown respectively in Figures 1 and 2, were employed for the tests. The scrubber, located at EPA/IERL-RTP, is a three-stage turbulent contact absorber (TCA) with 465 $m^3$/hr flue gas capacity (0.1 MW). No flyash was present in the flue gas, which was drawn from a gas-fired boiler and injected with pure $SO_2$ and HCl as required. The oxidizer consisted of a 30 cm diameter tower containing slurry at a depth of 5.5 m and was sparged with air from the tower bottom. A bleed stream of the slurry from the hold tank was directed to the clarifier and then processed by a rotary drum vacuum filter to remove the precipitated waste slurry. All filtrate was returned to the scrubber in order to maintain closed-loop operation. The system was manually controlled in a feed forward mode by maintaining a constant limestone stoichiometric ratio of moles of reagent added per mole of $SO_2$ absorbed (when lime was used, constant pH control was utilized). A small amount of excess reagent was also added to neutralize absorbed HCl gas during some tests.

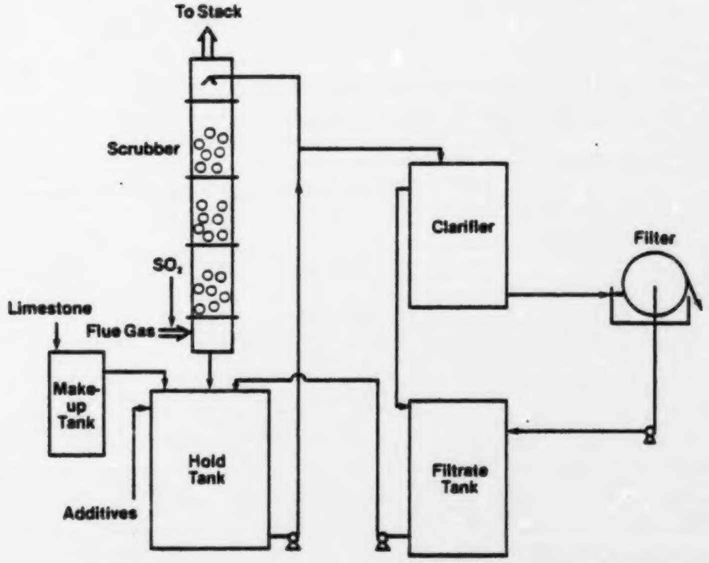

Figure 1. Flow diagram for single-loop natural oxidation tests in the 0.1 MW limestone pilot plant.

Granulated or powdered calcium chloride, magnesium chloride, or sodium chloride was added to the liquid inventory in order to bring the system to the desired $Cl^-$ level. HCl was (at specified times) injected into the inlet duct at predetermined levels in order to simulate flue gas generated by the combustion of high chloride coal. The limestone feed rate was adjusted manually by a trial and error method until steady-state stoichiometric ratios were achieved. Normally, each run consisted of at least 25 hours of continuous stable operation, after which scrubber performance and system conditions at each $Cl^-$ level were established by averaging operational data logged hourly.

The gas phase $SO_2$ concentration was monitored continuously using a DuPont 400 $SO_2$ analyzer and occasionally checked by wet gas titration. Liquid and solid samples of important species such as calcium, sulfite, sulfate, carbonate, magnesium, and sodium were analyzed.

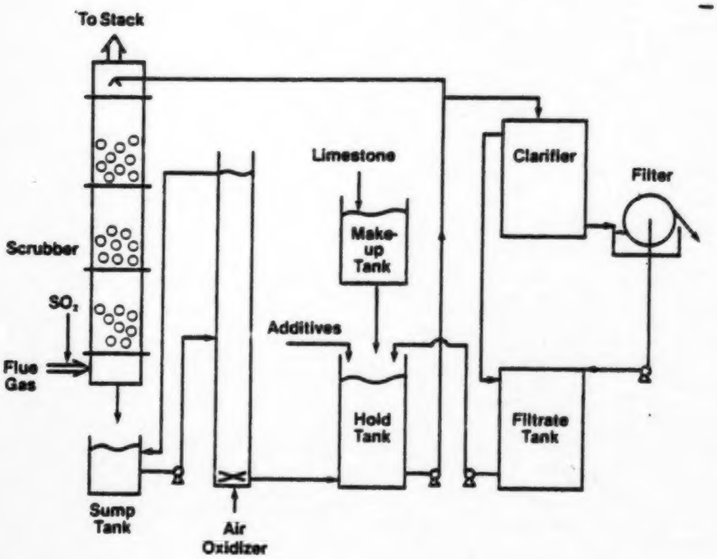

Figure 2. Flow diagram for in-loop forced oxidation tests in the 0.1 MW limestone pilot plant.

## METHOD OF APPROACH

The effect of $Cl^-$ on the FGD system was studied in three ways:

- All system parameters were held constant while the concentration of $Cl^-$ in the scrubbing liquor was increased.
- At a given $Cl^-$ concentration, either the liquid-to-gas ratio (L/G) or the limestone feed rate was increased until the base case $SO_2$ removal efficiency was obtained.
- The $Cl^-$ concentration was held constant while system parameters were varied individually.

For the third case, comparisons of the effects on $SO_2$ removal are difficult since the base case $SO_2$ removal changes significantly when L/G, limestone stoichiometry, or the absorber packing height are changed. Laslo and Bakke (4) outlined a method for comparing $SO_2$ removal efficiencies based on the logarithmic ratio of the fractional $SO_2$ remaining in the flue gas at high $Cl^-$, f, to the fractional $SO_2$ remaining at the base case conditions with no $Cl^-$, $f_B$.

Mathematically, this ratio, R, can be expressed as a percentage:

$$R = \frac{\ln(1 - f)}{\ln(1 - f_B)} \times 100.0 \qquad (1)$$

For all other tests, evaluation of effects was performed by examining system performance with and without $Cl^-$ addition or by quantitatively determining the L/G or excess limestone required to return to the base case.

Major areas of testing during the reporting period are summarized below:

- $Cl^-$ effects on the limestone FGD system utilizing the following salts alone or in combination:
  - Calcium chloride
  - Magnesium chloride
  - Sodium chloride

- Evaluation of methods to regain base case $SO_2$ removal efficiency at high calcium chloride concentrations including:
  - Increasing L/G
  - Increasing limestone feed rate
  - Adding organic acid
- Effects of calcium chloride on a lime based FGD system
- Effects of calcium chloride on a magnesia enhanced limestone FGD system
- Effects of calcium chloride on an organic acid enhanced limestone FGD system
- Washability evaluation of a gypsum cake using a horizontal belt filter

Each of these will be covered separately in the following text. By far, most testing was performed in a limestone based system using calcium chloride and thus will be treated in greater detail.

## RESULTS AND DISCUSSION

### $Cl^-$ EFFECTS ON LIMESTONE FGD SYSTEMS

### Calcium Chloride

Recycle slurry pH decreased as the concentration of calcium chloride increased. It has been shown that the change in pH closely follows the calculated equilibrium $H^+$ concentration in the natural oxidation mode of operation (1). The drop in pH in the forced oxidation mode was not significant until the $Cl^-$ concentration exceeded 50,000 ppm. Calculating the $H^+$ concentration during forced oxidation was not possible due to the stripping of $CO_2$ gas from the slurry. At the same $Cl^-$ concentration, the pH decrease in the natural oxidation mode was significantly more than operation in the forced oxidation mode.

A decrease in $SO_2$ removal efficiency was observed with the increase of calcium chloride concentration for both the natural and forced oxidation modes. As shown in Figure 3, the decrease was not as severe for the forced oxidation mode.

The natural oxidation data in Figure 3 was obtained using a high base case pH of 6.0 and a high limestone stoichiometry of 1.3-1.4 moles of $CaCO_3$

per mole of $SO_2$ absorbed. Additional tests were performed at a lower base case pH of 5.4-5.6, summarized in Table 1, and a series of tests run at high and low make-per-pass, summarized in Table 2. The make-per-pass, or the amount of $SO_2$ gas absorbed per liter of slurry, was minimized by simply removing the spheres from the TCA.

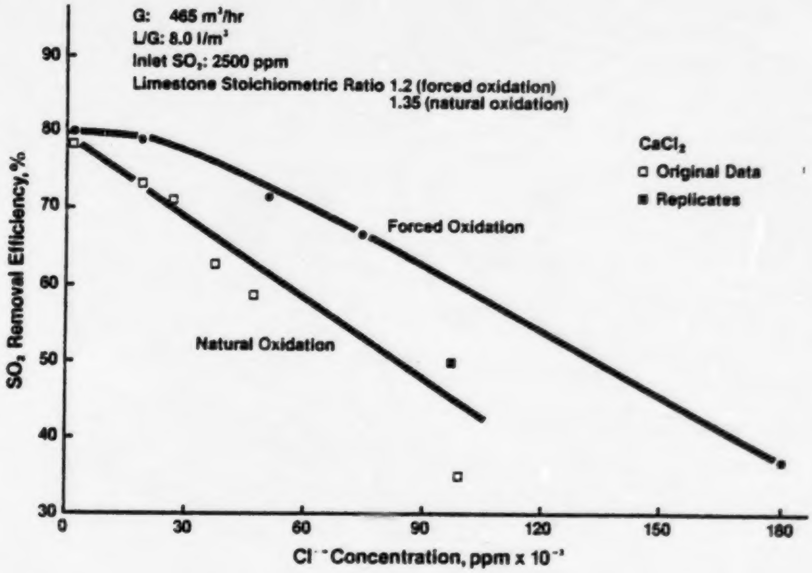

Figure 3. Comparison of natural and forced oxidation $SO_2$ removal efficiencies as a function of $Cl^-$.

Table 1. RESULTS OF LOW BASE CASE pH, NATURAL OXIDATION TESTS

| Test I.D. | Inlet $SO_2$ (ppm) | Cl Conc. (ppm) | pH | Limestone Stoich. (molar) | L/G (l/m³) | $SO_2$ Removal (%) | R from Eq. (1) (%) |
|---|---|---|---|---|---|---|---|
| NB-13 | 2500 | * | 5.6 | 1.16 | 8.0 | 68 | 100 |
| N2-4 | 2500 | 20,000 | 4.9 | 1.13 | 8.0 | 65 | 92 |
| N5-10 | 2500 | 50,000 | 4.6 | 1.16 | 8.0 | 60 | 80 |
| NB-14 | 700 | * | 5.4 | 1.11 | 3.0 | 77 | 100 |
| N2-HM1 | 700 | 20,000 | 5.2 | 1.07 | 3.0 | 75 | 94 |
| N5-HM5 | 700 | 50,000 | 5.0 | 1.13 | 3.0 | 68 | 77 |

* Base Case

Table 2. RESULTS OF HIGH/LOW MAKE-PER-PASS NATURAL OXIDATION TESTS

| Test I.D. | Inlet $SO_2$ (ppm) | Cl Conc. (ppm) | pH | Limestone Stoich. (molar) | L/G ($l/m^3$) | $SO_2$ Removal (%) | R from Eq. (1) (%) |
|---|---|---|---|---|---|---|---|
| | | | High Make-per-pass | | | | |
| NB-8 | 2500 | * | 5.8 | 1.2 | 11.2 | 89 | 100 |
| N5-HM1 | 2500 | 50,000 | 5.0 | 1.2 | 11.2 | 81 | 75 |
| NB-9 | 500 | * | 5.9 | 1.1 | 7.2 | 92 | 100 |
| N5-HM3 | 500 | 50,000 | 5.1 | 1.2 | 7.2 | 84 | 73 |
| | | | Low Make-per-pass | | | | |
| NB-10 | 2500 | * | 5.8 | 1.2 | 10.7 | 56 | 100 |
| N5-LM1 | 2500 | 50,000 | 4.9 | 1.1 | 10.7 | 47 | 77 |
| NB-11 | 500 | * | 5.9 | 1.1 | 4.5 | 52 | 100 |
| N5-LM3 | 500 | 50,000 | 5.4 | 1.2 | 4.7 | 43 | 77 |

* Base Case

Since it is difficult to compare tests at different base case conditions, R from Equation (1) was calculated for each test and is presented in both Tables 1 and 2. Figure 4 summarizes the values for R plotted as a function of the $Cl^-$ concentration for forced oxidation and the high base case pH natural oxidation data from Figure 3, as well as the data from Tables 1 and 2. It is apparent that R has a linear correlation with the $Cl^-$ concentration and is independent of inlet $SO_2$ concentration, make-per-pass, liquid holdup in the absorber, and liquid-to-gas ratio. Figure 4 also indicates that the intial base case pH is significant, since tests run with an initial pH of 6.0 (or a limestone stoichiometry of 1.3-1.4) have a slope significantly steeper than the tests run with an initial pH of 5.5-5.9 (or a limestone stoichiometry of 1.1-1.2).

In addition to decreases in $SO_2$ removal efficiency and pH, occasional decreases in the solids settling rate were observed in the natural oxidation mode at high $Cl^-$. Little effect of $Cl^-$ on solids settling was observed during the forced oxidation mode. Also, with the accumulation of calcium chloride, the relative saturation of gypsum in the scrubber system increased to levels conducive to scaling; however, scale was rarely observed in the pilot plant.

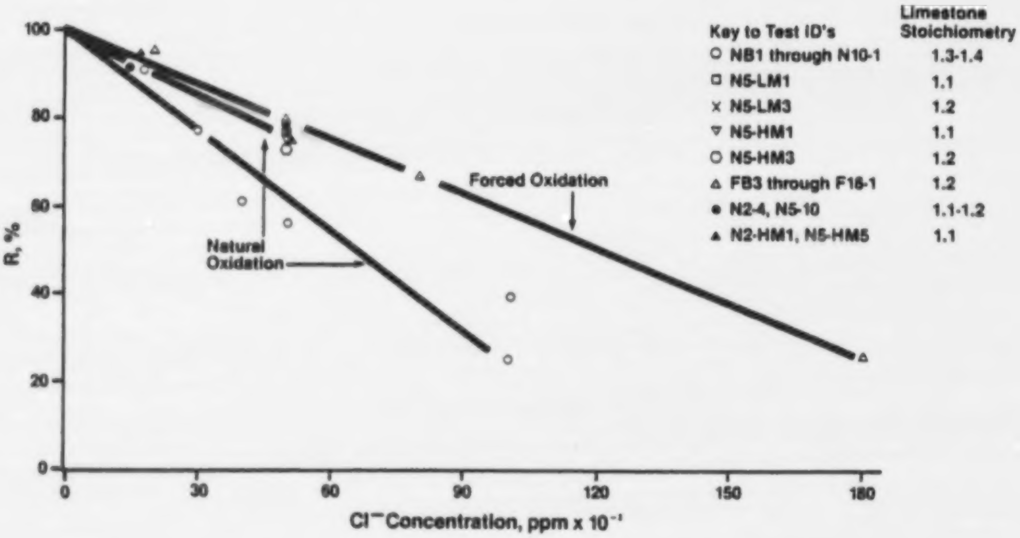

Figure 4. R, from Equation (1), vs. $Cl^-$ concentration.

## Magnesium Chloride

When using magnesium chloride as the source of $Cl^-$, a drop of system pH was observed at a rate similar to that obtained during calcium chloride testing, as the $Cl^-$ concentration increased. Figure 5 shows pH data for all tests as a logarithmic function of the sum of calcium and magnesium cations. It is apparent that the magnesium ion and the calcium ion behave similarly in affecting the equilibrium pH. The accumulation of magnesium chloride improved $SO_2$ removal efficiency when the $Cl^-$ concentration was below 40,000 ppm, as shown in Figure 6. However, a significant decrease in $SO_2$ removal efficiency occurred at $Cl^-$ concentrations greater than 50,000 ppm. Figure 6 also shows there was no effect of $Cl^-$ when a 50% molar mixture of magnesium chloride and calcium chloride was used — indicating that the positive effect of magnesium was cancelled by the negative effect of calcium chloride.

As shown in Figure 7, during forced oxidation, no significant effects of magnesium chloride on $SO_2$ removal efficiency were observed until the $Cl^-$ concentration exceeded 70,000 ppm, after which a slight drop in efficiency occurred. Also shown in Figure 7 is a more severe effect of the mixed calcium and magnesium salts due to the lack of magnesium enhancement during the forced oxidation mode.

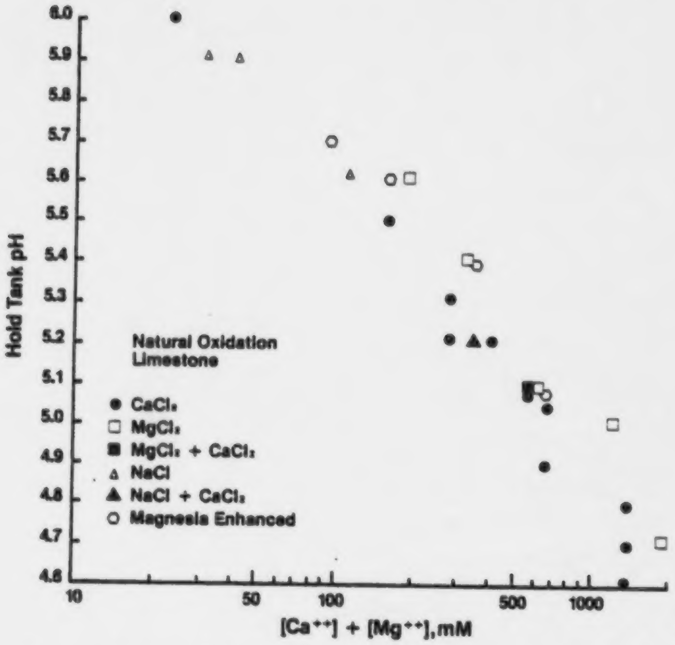

Figure 5. Comparison of hold tank pH's as a function of Mg$^{++}$ and Ca$^{++}$ cations.

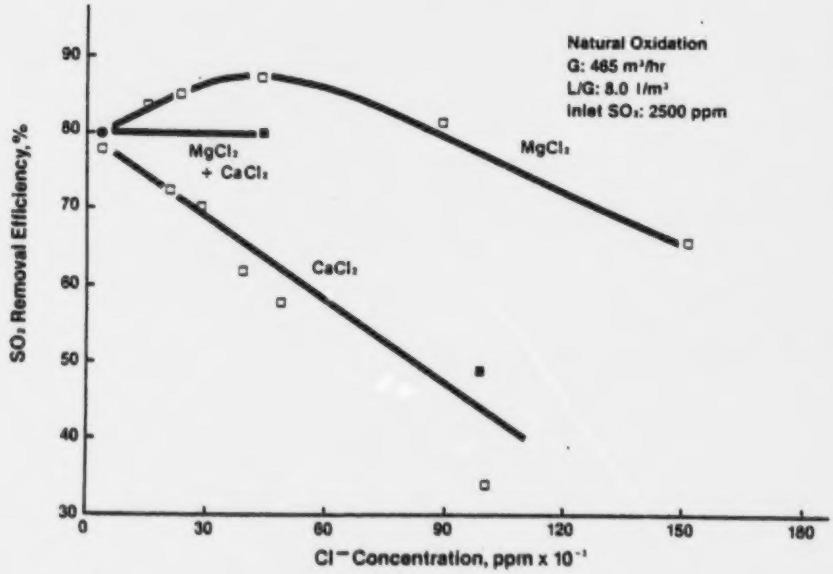

Figure 6. Comparison of natural oxidation $SO_2$ removal efficiencies as a function of Cl$^-$.

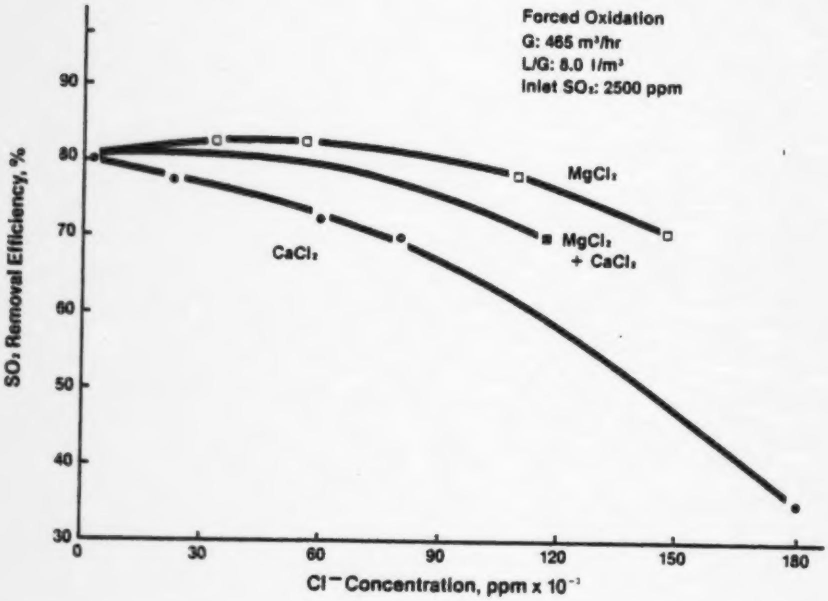

Figure 7. Comparison of forced oxidation $SO_2$ removal efficiencies as a function of $Cl^-$.

## Sodium Chloride

In the natural oxidation mode, no significant effects on $SO_2$ removal or pH were observed with the accumulation of sodium chloride until the $Cl^-$ concentration reached 50,000 ppm. The pH data are also plotted in Figure 5 which indicates that the pH is a function of the cations $Mg^{++}$ and $Ca^{++}$ only. As shown in Figure 8, when the $Cl^-$ concentration exceeded 50,000 ppm, drops in $SO_2$ removal were observed. When forced oxidation was employed, as shown in Figure 9, no effects on $SO_2$ removal were observed until the $Cl^-$ concentration exceeded 70,000 ppm.

## METHODS USED TO COUNTERACT THE EFFECT OF $Cl^-$ ON $SO_2$ REMOVAL EFFICIENCY

## Increasing the L/G Ratio

Test results show that at 40,000 ppm $Cl^-$ and a limestone stoichiometry of 1.3, the L/G ratio would have to be doubled in order to regain the base case $SO_2$ removal efficiency. Although never tested, the amount of L/G increase should be substantially lower at lower limestone stoichiometries due to the aforementioned reduced effects on $SO_2$ removal when low limestone stoichiometries are utilized.

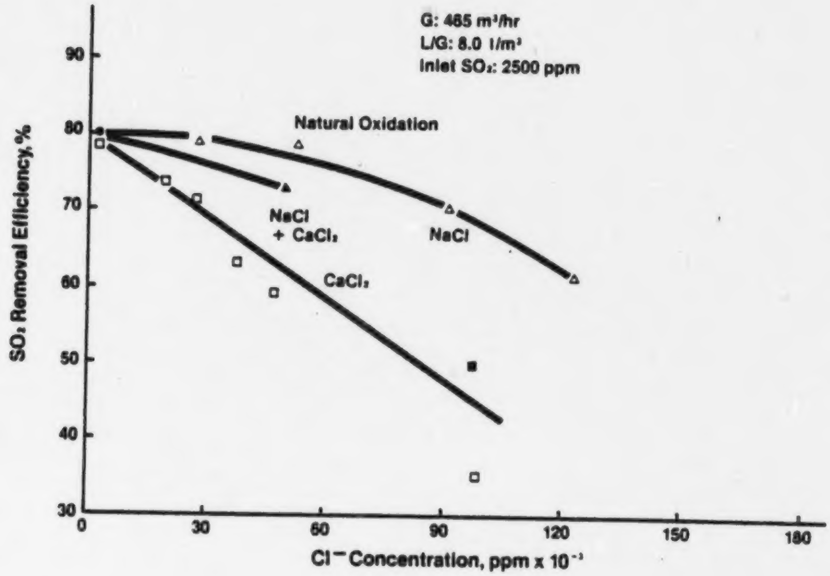

Figure 8. Comparison of natural oxidation $SO_2$ removal efficiencies as a function of $Cl^-$.

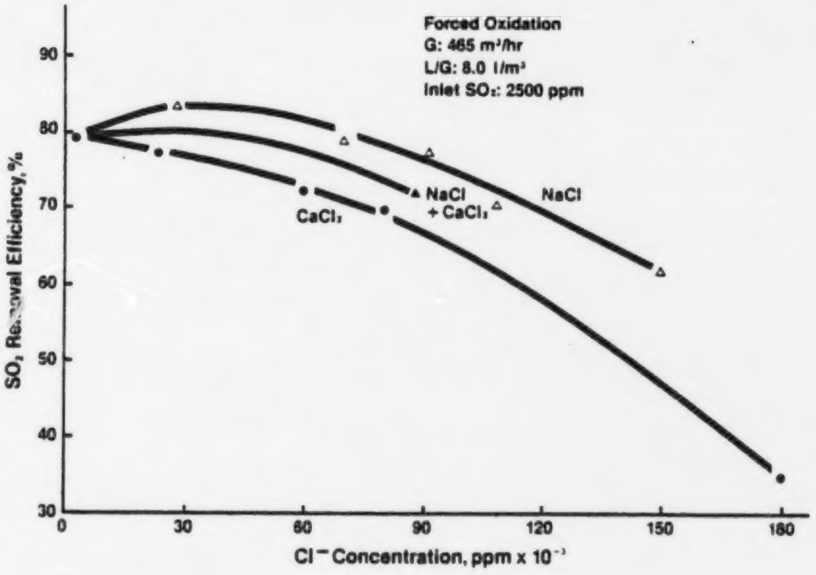

Figure 9. Comparison of forced oxidation $SO_2$ removal efficiencies as a function of $Cl^-$.

## Increasing the Limestone Feed Rate

Results of testing are summarized in Table 3. As can be seen, there is a significant difference in the amount of excess alkali required to restore base case $SO_2$ efficiency between the high and low limestone base case stoichiometry runs, but the quantity required in either case is unacceptably high.

Table 3. EXCESS LIMESTONE REQUIRED TO RESTORE BASE CASE $SO_2$ REMOVAL

| Base Case % $SO_2$ Removal | Inlet $SO_2$ (ppm) | Limestone Stoich. (molar) | $Cl^-$ Conc. (ppm) | Packing Height (cm) | Limestone Stoichiometry Required to Regain Base Case % $SO_2$ Removal (molar) |
|---|---|---|---|---|---|
| 80 | 2500 | 1.3-1.4 | 40,000 | 53 | 3.0 |
| 89 | 2500 | 1.16 | 50,000 | 65 | 1.6 |
| 56 | 2500 | 1.19 | 50,000 | 0 | 1.9 |
| 92 | 500 | 1.14 | 50,000 | 65 | 2.3 |
| 52 | 500 | 1.22 | 50,000 | 0 | 2.1 |

## Addition of Organic Acid

A mixture of organic acids, DBA, was added to the absorbing slurry at 50,000 ppm $Cl^-$ to determine the amount of acid required to restore the base case $SO_2$ removal efficiency. As seen in Figure 10, the amount required is only 9.2 meq/l. Further testing indicated that DBA is very effective in counteracting the effects of $Cl^-$ with forced oxidation, requiring only 9.4 meq/l to counteract the effect of $Cl^-$ at 160,000 ppm $Cl^-$.

## EFFECTS OF $Cl^-$ ON A LIME BASED FGD SYSTEM

The results of testing with lime are interesting in that the depression in $SO_2$ removal was identical to that of the limestone tests using high limestone stoichiometry, as shown in Figure 11. The lime tests were run at constant pH and a stoichiometric ratio approaching 1.0. Since pH control was used, only the absorber effluent pH declined when the $Cl^-$ concentration increased. When the inlet $SO_2$ concentration was lowered to 500 ppm, there was no noticeable effect of $Cl^{-2}$ on the $SO_2$ removal efficiency up to 100,000 ppm $Cl^-$.

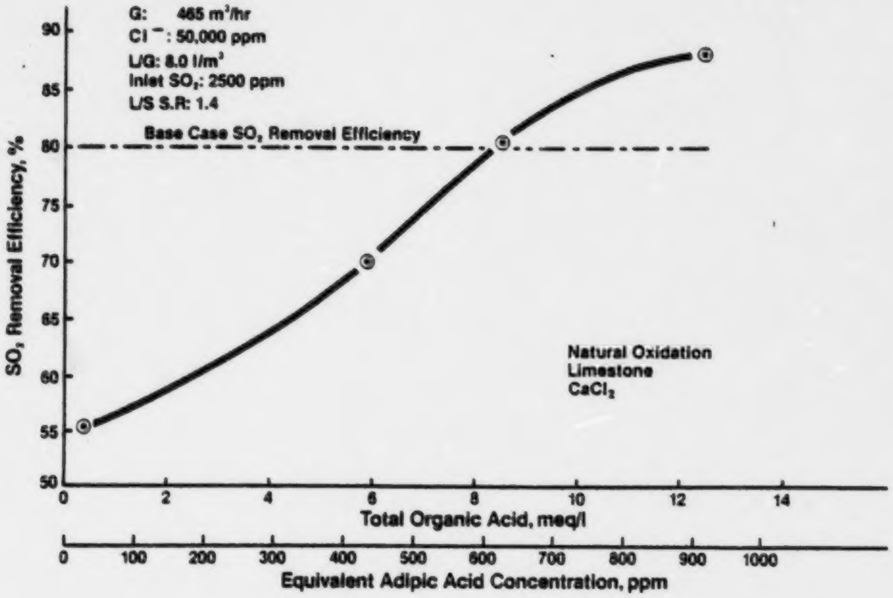

Figure 10. Effect of organic acid concentration on $SO_2$ removal efficiency at 50,000 ppm $Cl^-$ and natural oxidation.

## EFFECTS OF CALCIUM CHLORIDE ON A MAGNESIA ENHANCED FGD SYSTEM

Addition of magnesia to a conventional limestone FGD system increases the concentrations of two dissolved sulfite species, $SO_3^=$ and $MgSO_3^o$, which react with the absorbed $SO_2$ and enhance $SO_2$ removal. The accumulation of calcium chloride affects the magnesia enhanced limestone FGD system by reducing both $SO_3^=$ and $MgSO_3^o$ through chemical equilibrium effects. Pilot plant tests were conducted to evaluate the effects of calcium chloride on the performance of a magnesia enhanced limestone FGD system. Results indicate that when calcium chloride was initially added to the system, a sharp drop of $SO_2$ removal efficiency and a slight decrease in system pH were observed. The sharp drop in $SO_2$ removal reflected the reduction of $SO_3^=$ and $MgSO_3^o$ in the scrubbing liquor. As shown in Figure 12, further increases in the calcium chloride concentration resulted in less of an effect on $SO_2$ removal since the dissolved sulfite species have been depleted.

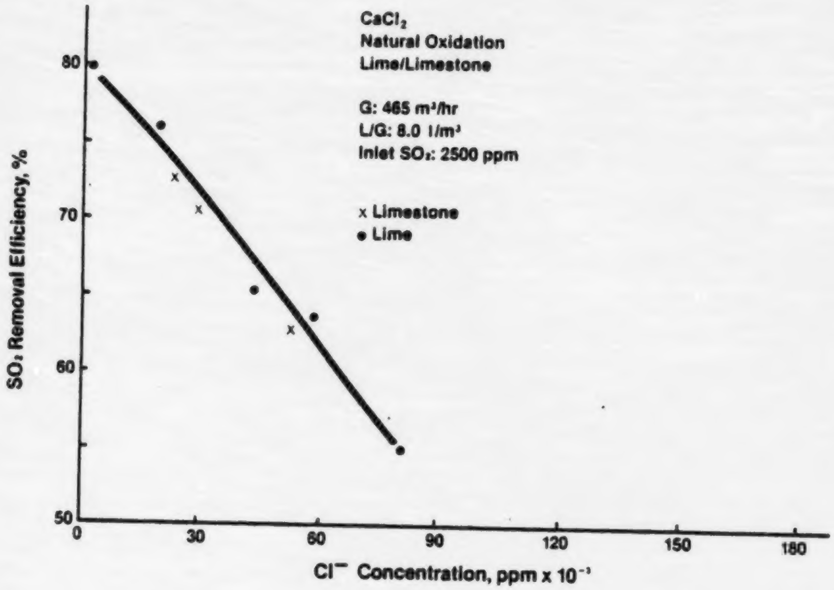

Figure 11. Effect of Cl$^-$ on SO$_2$ removal efficiency in a lime scrubber.

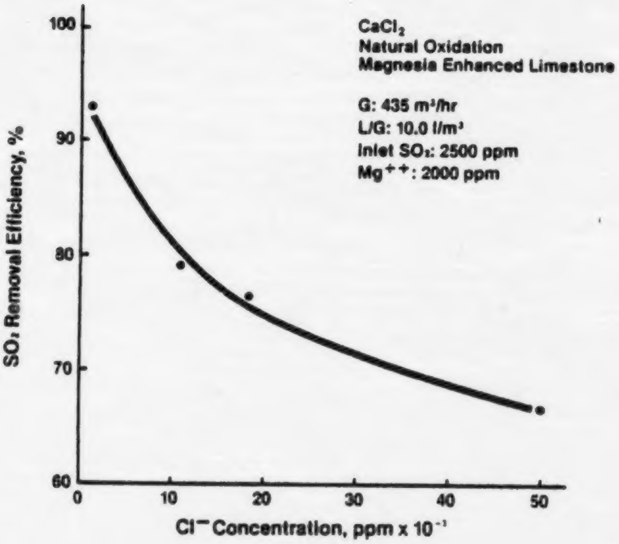

Figure 12. Effect of Cl$^-$ on SO$_2$ removal efficiency in a magnesia enhanced scrubber.

## EFFECTS OF CALCIUM CHLORIDE ON A DBA ENHANCED FGD SYSTEM

The operation of a DBA enhanced limestone FGD system has the advantage of high $SO_2$ removal efficiency, and low limestone stoichiometry. In order to simulate the DBA enhanced limestone scrubber, the base case pH was controlled at 5.2, limestone stoichiometry was less than 1.1, and $SO_2$ removal efficiency was 90% for both natural and forced oxidation tests. Short-term tests were utilized to evaluate the effects of $Cl^-$ on system performance. Long-term tests were conducted to evaluate DBA consumption and decomposition at high $Cl^-$ concentrations. $SO_2$ removal efficiency and system pH decreased in both the natural and forced oxidation modes. In order to maintain the base case $SO_2$ removal efficiency, DBA concentrations had to be increased as the $Cl^-$ concentration increased, as shown in Figure 13. In addition, plugging and scaling problems were encountered during the natural oxidation mode: hard scale formed on the scrubber bottom internals while operating at $Cl^-$ concentrations above 50,000 ppm and a phenomenon similar to "limestone blinding" was encountered while operating at a $Cl^-$ concentration of 120,000 ppm. There was no noticeable effect of high $Cl^-$ on the degradation rate of DBA, but an increase in the DBA coprecipitation rate was observed at high calcium chloride concentrations during natural oxidation testing as shown in Table 4.

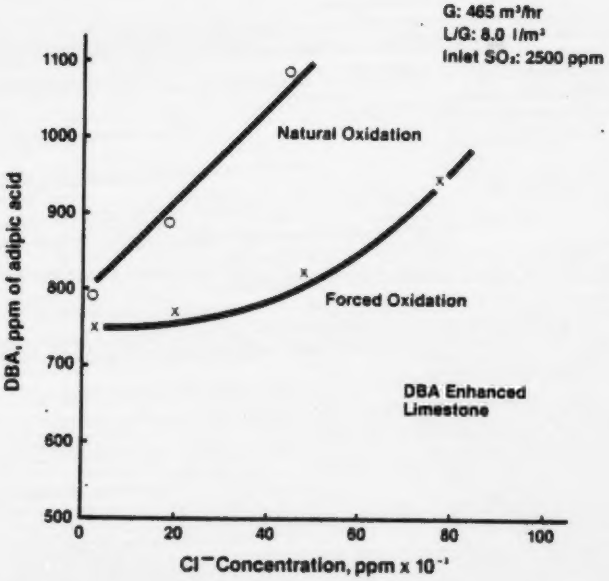

Figure 13. DBA concentration required to reach 90% $SO_2$ removal at high concentrations of $Cl^-$.

Table 4. COMPARISON OF UNACCOUNTABLE ORGANIC ACID LOSSES AT THE RTP LIMESTONE FGD PILOT PLANT

| | Natural Oxidation (g/hr) | Forced Oxidation (g/hr) |
|---|---|---|
| DBA losses at low Cl concentration (less than 8,000 ppm) | 7.4-8.0 | 14.4 |
| DBA losses at high $Cl^-$ concentrations* | 10.4 | 13.9 |

* $Cl^-$ = 30,000 ppm for natural oxidation
$Cl^-$ = 50,000 ppm for forced oxidation

## WASHABILITY EVALUATION OF GYPSUM CAKE USING A PILOT HORIZONTAL BELT FILTER

The marketability of gypsum produced from a forced oxidized FGD system is affected by its purity, especially with regard to dissolved solids. Gypsum generated from high $Cl^-$ FGD systems must be washed thoroughly to meet the purity specifications of wallboard manufacturers. A belt filter, with the potential of three-stage countercurrent washing, was utilized to determine the washability of gypsum cake produced during the DBA testwork described previously.

Results of these tests are shown in Figure 14 for both TDS and $Cl^-$. Also shown is the calculated theoretical washing efficiency obtained with ideal washing. These data indicate that the pilot belt filter approaches ideal washing. Chemical analysis of the resulting washed cake was performed at three different system $Cl^-$ concentrations. Results, shown in Table 5, indicate that commercial grade gypsum suitable for wallboard manufacturing could be produced from slurry containing up to 80,000 ppm $Cl^-$. Free moisture content was slightly high, but optimizing moisture was not in the scope of work.

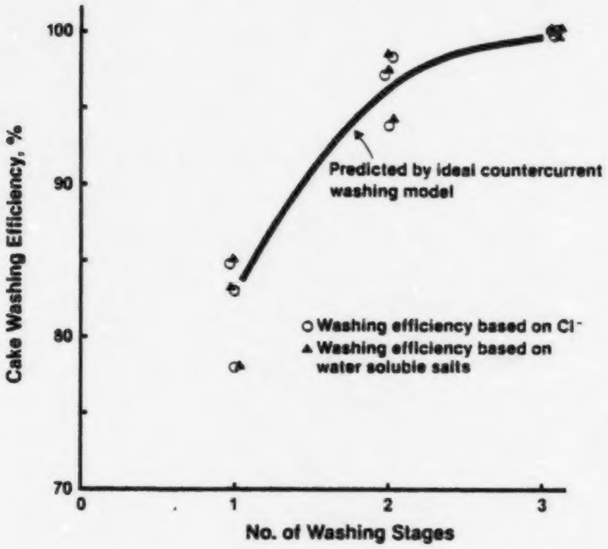

Figure 14. Performance of a belt filter with countercurrent washing and five wash displacements

Table 5. COMPARISON OF GYPSUM QUALITIES AFTER BELT FILTER WASHING

| | Required Quality* | Analysis of Sample from Slurry with Cl of | | |
|---|---|---|---|---|
| | | 50,000 ppm** | 80,000 ppm** | 120,000 ppm*** |
| Free Water, % | <10 | 14.4 | 15.4 | 15.7 |
| Combined Water, % | >19.8 | 21.4 | 19.6 | 20.7 |
| $CaSO_3 \cdot 1/2\ H_2O$, % | <2 | 1 | 1 | 2.1 |
| $CaCO_3$, % | <2 | 1 | 1 | 3.7 |
| CaO, % | ~31-33 | 32.6 | 32.6 | 33.8 |
| $SO_3$, % | >44 | 46.1 | 45.9 | 45.0 |
| Na, ppm | <75 | 5 | 5 | 5 |
| K, ppm | <75 | 5 | 5 | 5 |
| Mg, ppm | <50 | 8.0 | 6.0 | 8.0 |
| Cl, ppm | <120 | 90.6 | 98.6 | 292.4 |
| TDS, ppm | <600 | 136.3 | 147.5 | 451.8 |

* Specified by U.S. Gypsum for wallboard quality gypsum

** Washed with 5 displacement water and 3-stage countercurrent washing

*** Washed with 5 displacement water and 2-stage countercurrent washing

# CONCLUSIONS

- The $SO_2$ removal efficiency declined as calcium chloride accumulated in the limestone FGD system in both the natural and forced oxidation modes of operation. The decline was independent of absorber parameters such as liquid-to-gas ratio, packing height, and inlet $SO_2$ gas concentration within the ranges tested. Tests with natural oxidation and a base case pH of 6.0 had a greater drop in $SO_2$ removal than tests at a lower base case pH or tests run with forced oxidation. Significant decreases in $SO_2$ removal were also observed when lime was substituted for limestone in the natural oxidation mode.

- The effect of $Cl^-$ is cation dependent. Evidence from conventional limestone testing indicates that below 50,000 ppm $Cl^-$, $SO_2$ removal is not adversely affected when $Mg^{++}$ or $Na^+$ is the cation.

- The system pH decreased as the $Cl^-$ concentration increased when $Mg^{++}$ or $Ca^{++}$ was the cation in both the natural and forced oxidation modes. In the natural oxidation mode, pH was found to follow equilibrium $H^+$ concentrations. No significant change in system pH was observed when $Na^+$ was the cation.

- The accumulation of calcium chloride depressed $SO_2$ removal efficiency which could be restored by adding excess limestone, small amounts of the organic acid DBA, or by increasing the liquid-to-gas ratio.

- The accumulation of calcium chloride in a magnesia enhanced limestone FGD system significantly reduced $SO_2$ removal efficiencies due to equilibrium effects on dissolved alkalinity.

- The concentration of organic acid in a DBA enhanced limestone FGD system had to be increased as the calcium chloride concentration increased in order to maintain a constant $SO_2$ removal efficiency. An increase in the DBA coprecipitation rate was measured at high calcium chloride concentrations, but no increase in the DBA degradation rate was measured.

- Gypsum, washed with a three-stage countercurrent belt filter, met each specification required for wallboard manufacturing (except free moisture) with feed slurry $Cl^-$ concentrations as high as 80,000 ppm.

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2. Hargrove, O.W., et al., "The Effects of Process Water Selection on Lime-Limestone Flue Gas Desulfurization Chemistry," Electric Power Research Institute Report CS-2451, July 1982.

3. Chang, J.C.S.,"Pilot Plant Tests of Chloride Ion Effects on Wet FGD System Performance," Draft Final Report, EPA/Acurex Contract No. 68-02-3648, June 1983.

4. Laslo, D., and E. Bakke, "The Effect of Dissolved Solids on Limestone FGD Scrubbing Chemistry," Presented at the ASME 1983 Joint Power Generation Conference, September 27, 1983.

# MODELING OF $SO_2$ REMOVAL BY LIMESTONE SLURRY SCRUBBING: EFFECTS OF CHLORIDES

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## ABSTRACT

A model of limestone slurry scrubbing with staged contacting has been developed by integrating gas/liquid mass transfer of $SO_2$, $CO_2$, and $O_2$ and dissolution of limestone and calcium sulfite solids. The model was used to predict $SO_2$ removal as a function of NaCl and $CaCl_2$ accumulation in the solution. Experimental data from three different pilot plants were accurately simulated. Chloride accumulation reduces $SO_2$ removal by its effect on the $SO_2$ hydrolysis equilibrium. Calcium accumulation reduces $SO_2$ removal by its effect on $SO_3^=$ and $HCO_3^-$ in the scrubber solution. Sulfite oxidation in the scrubber can obscure the effects of $CaCl_2$ accumulation. The model predicts the effect of dibasic acid (glutaric) on $SO_2$ removal with solutions containing 0.7 M $CaCl_2$.

## INTRODUCTION

Limestone slurry scrubbing is the most widely used flue gas desulfurization process. Typically it includes a countercurrent spray scrubber with a large slurry recycle from a hold tank and a slurry bleed to solids dewatering and waste disposal. The scrubber is usually designed to include gas/liquid mass transfer of $SO_2$, $CO_2$, and $O_2$, limestone ($CaCO_3$) dissolution, and calcium sulfite ($CaSO_3$) dissolution. The hold tank is designed for dissolution of the rest of the $CaCO_3$ and crystallization of $CaSO_3$ and calcium sulfate ($CaSO_4$). In some systems, oxidation of sulfite to sulfate is forced by adding air to the hold tank.

## BACKGROUND FOR SCRUBBER MODELING

Early effort in simulating this process was limited to a model based on gas/liquid/solid equilibria (Lowell et al., 1970). Rochelle and King (1977) integrated the $SO_2$ mass transfer rate over the changing gas-phase concentration in a column, assuming constant dissolved alkalinity and no $SO_2$ back-pressure. Performance data obtained in 10-MW scrubbers have been correlated by McMichael et al. (1976) and Head (1977).

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Mehta (Mehta and Rochelle, 1983; Mehta, 1982) integrated $SO_2$ gas/liquid mass transfer and $CaCO_3$ dissolution as a function of changing gas and solution composition across the length of a column. His model for $SO_2$ mass transfer included both gas- and liquid-phase resistance and simulated liquid-phase mass transfer by approximate surface renewal theory with equilibrium reactions (Chang and Rochelle, 1982a,b; Weems, 1981). $CaCO_3$ dissolution was modeled by mass transfer with equilibrium reactions using film theory (Chan and Rochelle, 1982; Toprac and Rochelle, 1982; Rochelle et al., 1983). Solution equilibria were calculated by the Bechtel-modified Radian equilibrium program (Epstein, 1975).

This work extends the effort of Mehta by adding gas/liquid mass transfer of $CO_2$ and $O_2$ and $CaSO_3$ dissolution by mass transfer with equilibrium reactions (Tseng and Rochelle, 1983). The equilibrium procedures used by Mehta have been simplified, and the model has been extended to include countercurrent staged contacting. The model used in this work does not include simulation of the hold tank, and calculates $SO_2$ removal from a specified scrubber inlet solids and solution composition.

## BACKGROUND FOR EFFECTS OF CHLORIDES

Extensive experimental work has been performed on the effects of chlorides on $SO_2$ removal in limestone slurry scrubbing. HCl from flue gas and chloride salts from makeup water can accumulate as dissolved $CaCl_2$, NaCl, or $MgCl_2$ in the scrubber system. Pilot plant work on these effects has been performed at four facilities:

1) EPA-RTP - Research Triangle Park, North Carolina, 7.8 $m^3$/min TCA scrubber, work performed by Acurex and sponsored by EPA and Peabody (Chang and Laslo, 1983; Acurex, 1983; Laslo et al., 1983).

2) Radian - Austin, Texas, 0.02 $m^3$/min bubbler, work performed by Radian Corporation and sponsored by the Electric Power Research Institute (Jarvis et al., 1983 a,b).

3) CE - Windsor, Connecticut, 34 $m^3$/min, spray tower, work performed and sponsored by Combustion Engineering (Rader et al., 1982).

4) Shawnee - Paducah, Kentucky, 780 $m^3$/min spray/tray scrubber, work performed by TVA, Radian, and Babcock and Wilcox (B&W) and funded by TVA, EPRI, and B&W (Downs and Robards, 1983).

The data from these four sources are not in complete agreement on the effects of chloride. With forced oxidation, 0.7 M $CaCl_2$ (50,000 ppm $Cl^-$) reduced $SO_2$ removal by comparable amounts at EPA-RTP (80-85 to 73%), Radian (80 to 75%), and Shawnee(66 to 58%). However, with natural oxidation, 0.7 M $CaCl_2$ reduced $SO_2$ removal more at EPA-RTP (80 to 60%) than at Radian (75 to 70%) or Shawnee (65 to 54%) and had no effect at CE (50 to 50%).

This paper is an attempt to resolve these and other apparent discrepancies in the experimental data by simulation of $SO_2$ removal with the integrated scrubber model. Most of the simulation has concentrated on the

EPA-RTP and Radian data with effects of $CaCl_2$ and NaCl. The Shawnee data were unavailable at the time of this analysis. Data on the effects of $MgCl_2$ were not simulated because of a fault in the equilibrium data base for $Mg^{++}$ activity coefficients.

## MODEL DESCRIPTION

The performance of $CaCO_3$ slurry scrubbing has been modeled by numerical solution of differential and algebraic equations representing three processes of mass transfer enhanced by equilibrium reactions:

1) $SO_2$, $CO_2$, and $O_2$ absorption/desorption
2) Limestone ($CaCO_3$) dissolution
3) Calcium sulfite ($CaSO_3$) dissolution

These three processes depend on and affect the solution concentrations of total $SO_2$, $SO_3$, $CO_2$, and Ca. Scrubber performance has been determined by solution of the rate and material balance equations to give gas and solution composition at every point in a staged scrubber.

## SOLUTION EQUILIBRIA AND DIFFUSIVITIES

Rigorous solution equilibria were calculated once for the scrubber inlet solution by the Bechtel-modified Radian Equilibrium Program (BMREQ) (Lowell et al., 1970; Epstein, 1975). These equilibrium results were then simplified to eliminate ion pairs and incorporate activity coefficients into the equilibrium constants. For example, the simplified equilibrium constant for the reaction,

$$HSO_3^- \rightleftharpoons H^+ + SO_3^=$$

$$K = [H^+][SO_3^=]/[HSO_3^-] \qquad (1)$$

is given using concentrations by BMREQ at the ionic environment of a given simulation,

$$K = \frac{[H^+]([SO_3^=] + [CaSO_3^\circ] + [MgSO_3^\circ]\ldots)}{([HSO_3^-] + [CaHSO_3^+]\ldots)} \qquad (2)$$

With the simplified equilibria, the species $SO_3^=$ includes the concentrations of $SO_3^=$, $CaSO_3^\circ$, and other sulfite ion pairs in the rigorous equilibria. The simplified equilibria included only 13 solution species: $H^+$, $OH^-$, $SO_2$, $HSO_3^-$, $SO_3^=$, $CO_2$, $HCO_3^-$, $CO_3^=$, $H_2A$, $HA^-$, $A^=$, $HSO_4^-$, and $SO_4^=$. In addition, $Ca^{++}$, $Na^+$, and $Cl^-$ were included for charge balance, but participated in no solution equilibria. Mass balance in this system is represented by the components $SO_2$ ($SO_3^= + HSO_3^- + SO_2$), $CO_2$ ($CO_3^= + HCO_3^- + CO_2$), $SO_4^=$ ($SO_4^= + HSO_4^-$), $H_2A$ ($A^=$, $HA^-$, $H_2A$; e.g., adipic acid), $Ca^{++}$, $Na^+$, and $Cl^-$. The use of simplified equilibria is a good approximation to the extent that ionic strength and $Ca^{++}$ concentration do not change significantly across the scrubber.

BMREQ was modified to include the solution species $CaHSO_3^+$ and $NaHSO_3^\circ$ with the rigorous equilibria:

$$\frac{a_{Ca^{++}}\ a_{HSO_3^-}}{a_{CaHSO_3^+}} = 0.073 \tag{3}$$

$$\frac{a_{Na^+}\ a_{HSO_3^-}}{a_{NaHSO_3^\circ}} = 2.53 \tag{4}$$

With these equilibria, the program accurately predicts the solubility of $SO_2$ gas at $1.8 \times 10^{-3}$ atm measured by Radian (Jarvis et al., 1983b) in NaCl and $CaCl_2$ solutions with up to 4 M chloride.

Based on data by Tseng and Rochelle (1983), the $CaSO_3 \cdot \frac{1}{2}H_2O$ solubility product has been reduced by 75% to give:

$$K_{sp,CaSO_3} = a_{SO_3^=}\ a_{Ca^{++}} = 2.637\text{x}10^{-7}\ M^2 \tag{5}$$

Based on data by Chan and Rochelle (1982), the effective solubility of limestone is limited by sulfite with the apparent equilibrium,

$$K_{sp,CaCO_3 \cdot CaSO_3} = a^2_{Ca^{++}}\ a_{SO_3^=}\ a_{CO_3^=} = 8.95\text{x}10^{-18}\ M^4 \tag{6}$$

Oxygen gas solubility was given by the equilibrium (Int. Crit. Tables):

$$H_{O_2} = P_{O_2}/[O_2] = 1058.7 \text{ atm/M at } 50^\circ\text{C} \tag{7}$$

A set of estimated diffusion coefficients was taken from Mehta and Rochelle (1983). Diffusivities for use with the simplified equilibria were calculated as weighted averages based on concentrations from rigorous equilibria. For example,

$$D_{SO_3^=}(\text{simplified}) = (\Sigma D_j[j])/\Sigma[j] \tag{8}$$

where $j = SO_3^=$, $CaSO_3^\circ$, $MgSO_3^\circ$. Diffusivities for use in gas/liquid mass transfer were calculated as weighted averages of their square roots:

$$D^{0.5}_{SO_3^=} = (\Sigma D_j^{0.5}[j]/\Sigma[j]) \tag{9}$$

## GAS/LIQUID MASS TRANSFER OF $SO_2$, $CO_2$, AND $O_2$

$SO_2$ and $O_2$ absorption and $CO_2$ desorption/absorption were modeled by two-film theory with an approximation of surface renewal theory to estimate enhancement of liquid-phase diffusion by equilibrium reactions (Chang and Rochelle, 1982a,b; Mehta and Rochelle, 1983). The total flux of a component (such as $[SO_2]_T = [SO_2] + [HSO_3^-] + [SO_3^=]$) in the liquid film is given in approximate surface renewal theory by:

$$\text{Flux} = \frac{k_\ell^\circ}{D^{0.5}_{SO_2}} \Sigma D_j^{0.5} \Delta[j] \tag{10}$$

where $\Delta[j]$ is the concentration difference of a single species across the film, $[j]_i - [j]_b$.

The flux of $SO_2$ through the gas film is given by:

$$\text{Flux}_{SO_2} = k_g(P_{SO_2} - P_{SO_{2,i}}) \tag{11}$$

This must be equal to the flux of $SO_2$ plus sulfate through the liquid film:

$$k_g(P_{SO_2} - P_{SO_{2,i}}) = \frac{k_\ell^\circ}{D^{0.5}_{SO_2}} (\Sigma D_j^{0.5}\Delta[SO_{2,j}] + \Sigma D_j^{0.5}\Delta[SO^=_{4,j}]) \tag{12}$$

where $SO_{2,j}$ includes $SO_2$, $HSO_3^-$, and $SO_3^=$, and $SO^=_{4,j}$ includes $SO_4^=$ and $HSO_4^-$. The solution and gas concentrations of $SO_2$ at the gas/liquid interface must be in equilibrium:

$$[SO_2]_i = H\ P_{SO_{2i}} \tag{13}$$

The flux of $CO_2$ is obtained from Eq. 10 with j including $CO_2$, $HCO_3^-$, and $CO_3^=$. Gas film resistance is neglected for $CO_2$ giving:

$$[CO_2]_i = H\ P_{CO_2} \tag{14}$$

The finite-rate reaction of $CO_2$, $H_2O$, $H^+$, and $HCO_3^-$ is assumed to be at equilibrium in the liquid film.

Absorption of $O_2$ is assumed to occur with instantaneous oxidation of sulfite at the gas/liquid interface. The rate of absorption is assumed to be a constant factor, E, times the rate equivalent to physical absorption of oxygen. Therefore both oxygen absorption and sulfite oxidation are given as the flux of the component sulfate ($SO_4^=$ and $HSO_4^-$):

$$\text{Flux}_{SO_4^=} = \frac{k_\ell^\circ}{D_{SO_2}^{0.5}} \left(D_{SO_4^=}^{0.5} \Delta[SO_4^=] + D_{HSO_4^-}^{0.5} \Delta[HSO_4^-]\right) = 2\ E \frac{k_\ell^\circ}{D_{SO_2}^{0.5}} D_{O_2}^{0.5} H_{O_2} P_{O_2} \tag{15}$$

The flux of other non-volatile components and charge is taken to be zero. Therefore, Eq. 10 gives relationships for adipic acid ($H_2A$, $HA^-$, $A^=$) and for all charged species where [j] is equal to the product of charge and molarity.

When combined with solution equilibria for acid/base reactions, Eqs. 10 to 15 can be solved numerically to obtain bulk and interface compositions and fluxes of $CO_2$, $SO_2$, and $SO_4^=$ ($O_2$). These calculations require specification of bulk solution component concentrations and the system parameters $k_\ell^\circ$, $k_g$, and E, or an equivalent set of information.

## SOLID/LIQUID MASS TRANSFER

Limestone and $CaSO_3$ dissolution are both modeled as steady-state mass transfer between the solid surface and the bulk solution (Chan and Rochelle, 1982; Mehta and Rochelle, 1983; Tseng and Rochelle, 1983). In this case the flux of a component is proportional to the first power of the diffusivity, and is given in terms of the film thickness as:

$$\text{Flux} = \frac{1}{\delta} \Sigma D_j\ \Delta[j] \tag{16}$$

For limestone, the rate of dissolution is the flux of $Ca^{++}$ or of carbonate components ($CO_3^=$, $HCO_3^-$). The reaction of $H^+$ with $HCO_3^-$ is assumed to be negligible in the boundary layer, so $CO_2$ is not included as a diffusing species. By material balance, the flux of $Ca^{++}$ must be equal to the carbonate flux. The fluxes of charge and of the components sulfite, sulfate, and adipic acid are zero. The solution at the limestone surface is assumed to be saturated to calcite, giving:

$$[Ca^{++}]_s[CO_3^=]_s = K_{sp,calcite} \tag{17}$$

In the presence of sulfite, the solution at the limestone surface has the apparent composition given by Eq. 6. In both cases the $K_{sp}$ values are adjusted to reflect the effect of activity coefficients and ion pairs.

For $CaSO_3$ dissolution, the dissolution rate is the flux of $Ca^{++}$ which must be equal to the flux of sulfite ($SO_3^=$, $HSO_3^-$, $SO_2$) plus the flux of sulfate ($SO_4^=$, $HSO_4^-$). By stoichiometry, the ratio of sulfate and sulfite fluxes must be equal to ratio of $CaSO_4$ and $CaSO_3$ in the hemihydrate solid solution (up to 20% $CaSO_4$). The fluxes of carbonate ($CO_3^=$, $HCO_3^-$), adipic acid ($A^=$, $HA^-$, $H_2A$), and total charge must be zero. At the $CaSO_3$ surface, the solution is saturated with $CaSO_3$ as given by Eq. 5.

If the bulk solution composition is given, flux for limestone or $CaSO_3$ dissolution can be found by numerical solution of the set of equations representing the fluxes, solid/liquid equilibria, and acid/base solution equilibria. The parameters $CaCO_3$ reactivity and $CaSO_3$ reactivity are specified to give the effective combination of solid surface area and film thickness in the scrubber. Quantification of these parameters will be described later. Both of the solid dissolution models permit apparent crystallization if the driving force is negative. However, these results are not rigorous, and care should be taken when using calculated results when $CaSO_3$ crystallization occurs in the scrubber.

SCRUBBER INTEGRATION

The results calculated in this paper assume a countercurrent scrubber with several stages of contacting. In each contacting stage, the solution is well-mixed and the gas is in plugflow. In a single stage the liquid composition is equal throughout to the outlet liquid composition; therefore, the rates of $CaSO_3$ and $CaCO_3$ dissolution are constant. However, the gas composition varies, and the rate of gas/liquid mass transfer must be numerically integrated.

With a guessed outlet solution composition and known outlet gas composition for a single stage, the inlet gas composition is determined by numerically integrating the three differential equations:

$$\frac{dP_i}{dN_g} = \frac{k_\ell^\circ \, (\Sigma D_j^{0.5} \Delta[j])_i}{k_g \, D_{SO_2}^{0.5}} \qquad (18)$$

where $i = SO_2$, $CO_2$, and $O_2$ $(SO_4^{=})$. $N_g$ is the number of gas-phase mass transfer units and can be defined by:

$$N_g = \frac{k_g a \, ZP_T}{G} \qquad (19)$$

For each step in the integration the values of $\Sigma D_j^{0.5} \Delta[j]$ are calculated by solving numerically the algebraic equations for fluxes and equilibria in gas/liquid mass transfer.

For each stage in the scrubber the following algebraic equations were solved numerically to determine the outlet liquid composition from a given inlet liquid composition and outlet gas composition:

$$\frac{L}{G} \left( [SO_4^{=}]_{T,out} - [SO_4^{=}]_{T,in} \right) = 2 \left( P_{O_{2,in}} - P_{O_{2,out}} \right) \qquad (20)$$

$$\frac{L}{G}\left([SO_2]_{T,out} - [SO_2]_{T,in}\right) = (P_{SO_{2,in}} - P_{SO_{2,out}})$$

$$-2(P_{O_{2,in}} - P_{O_{2,out}}) + K_{CaSO_3} N_g \frac{L}{G} (\Sigma D_j \Delta[SO^{=}_{3,j}]) \qquad (21)$$

$$\frac{L}{G}\left([CO_2]_{T,out} - [CO_2]_{T,in}\right) = (P_{CO_{2,in}} - P_{CO_{2,out}}) + K_{CaCO_3} N_g \frac{L}{G}(\Sigma D_j \Delta[CO^{=}_{3,j}] \qquad (22)$$

$$([Ca^{++}]_{out} - [Ca^{++}]_{in})/N_g = K_{CaSO_3} \Sigma D_j \Delta[SO^{=}_{3,j}] + K_{CaCO_3} \Sigma D_j \Delta[CO_{3,j}] \qquad (23)$$

At each stage an initial guess of outlet composition was generated. Then the gas-phase integration was performed and a library routine (IMSL/ZSPOW) was used to solve the nonlinear Eqs. 20 to 23.

Since outlet gas composition is not usually known with a multistage contactor, an additional convergence loop is needed. With a guessed value of outlet $SO_2$ gas composition, each stage of the scrubber is solved from top to bottom. The scrubber inlet $SO_2$ gas composition is compared with its specified value, and the guess of outlet gas composition is updated. This procedure continues until satisfactory convergence is achieved.

## SOLIDS REACTIVITY PARAMETERS

The $CaSO_3$ and $CaCO_3$ reactivity parameters used in Eqs. 20 to 23 are defined such that:

$$K_{CaCO_3} = \frac{AT}{\delta} \qquad (24)$$

where A is the solids surface area per volume solution, $\delta$ is the apparent film thickness, equal to particle radius for particles less than 10 μm in diameter, and T is the slurry residence time (sec) in the scrubber per transfer unit. These reactivity parameters can be derived from particle size distributions or from batch dissolution data. Limestone reactivity is given by:

$$K_{CaCO_3} = \left(\frac{U}{t\Sigma D_j \Delta[CO^{=}_{3,j}]}\right) C_s T \qquad (25)$$

where $C_s$ is the total calcium solids concentration in the slurry (M) and the relative reactivity ($U/t\Sigma D_j \Delta[CO_{3,j}]$) is calculated by the method of Toprac and Rochelle (1982) from batch dissolution data. Figure 1 gives the relative reactivities of the limestones used at EPA-RTP and Radian for most of the high chloride studies. These values were calculated from values measured by batch dissolution at pH 4.0 with $CO_2$ sparging (Radian) or at pH 5 with $N_2$ sparging (EPA-RTP).

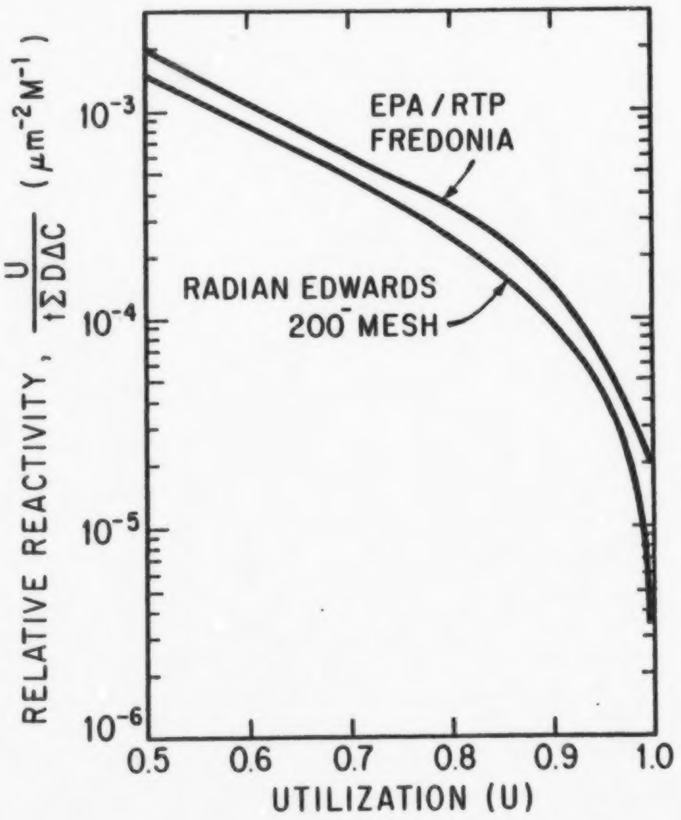

Figure 1. Relative Reactivity Versus Utilization for Radian and EPA-RTP Limestones.

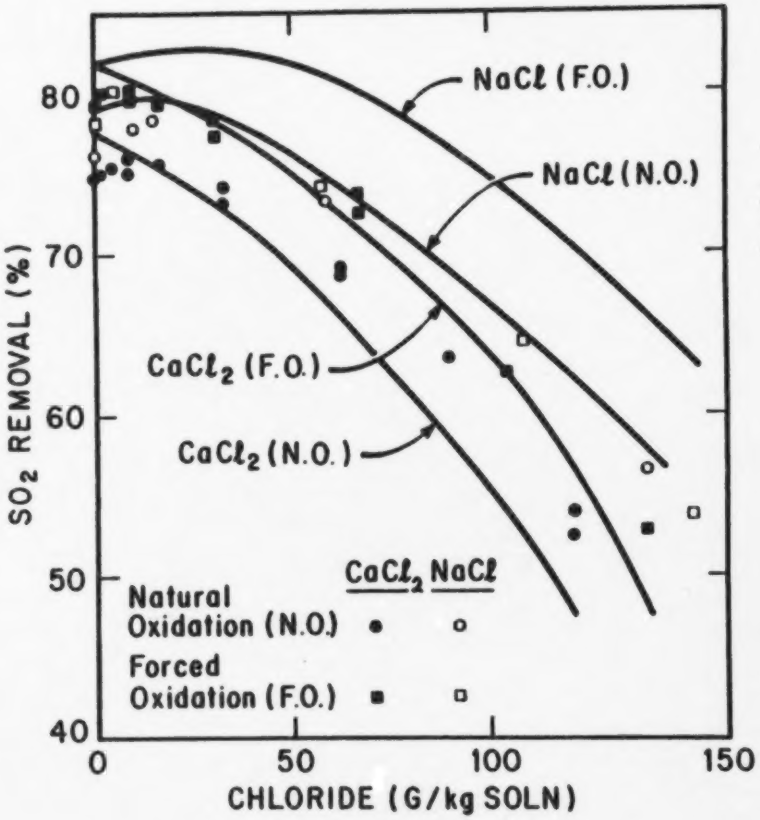

Figure 2. Simulation of Radian Data, Curves Calculated Using Conditions in Table 1.

# RESULTS

## INPUT SPECIFICATIONS

The following input data and parameters are needed to model a specific scrubbing operation:

1. Gas and solution inlet composition
2. Liquid to gas ratio, L/G
3. Number of contacting stages and gas-phase transfer units, $N_g$
4. Ratio of liquid and gas film mass transfer coefficients, $k^\circ_\ell/k_g$
5. $CaCO_3$ and $CaSO_3$ reactivity, $K_{CaCO_3}$ and $K_{CaSO_3}$
6. Oxidation enhancement factor, E

Table 1 outlines the values of parameters used to model the Radian, EPA-RTP, and CE data. Wherever possible actual pilot plant data for inlet gas and solution compositions and for L/G were input to the model. $N_g$ and $k^\circ_\ell/k_g$ were adjusted as necessary to simulate $SO_2$ removal for each set of liquid and gas flowrates and scrubber intervals. Where possible, values of $CaCO_3$ reactivity were selected that would be near the values estimated from measured relative reactivity, scrubber liquid holdup, and slurry concentration. $CaSO_3$ reactivity was chosen to be zero with forced oxidation, and up to $10^5$ sec/cm$^2$ with natural oxidation. The oxidation enhancement factor was adjusted to simulate observed levels of natural oxidation and varied from 1 to 7, consistent with kinetics observed by Ulrich (1983).

## RADIAN

Figure 2 gives calculated $SO_2$ removal for Radian results in the one-stage bubbler with NaCl and $CaCl_2$. $N_g$ was set at 2.2 to simulate observed $SO_2$ removal by $Na_2CO_3$ scrubbing. The parameter $k^\circ_\ell/k_g$ was estimated to be 0.28 atm/M from observed $SO_2$ removal by HCl solution; however, an adjusted value of 0.9 atm/M was necessary to simulate correctly $SO_2$ removal with $CaCO_3$ slurry and forced oxidation. The value of $k^\circ_\ell/k_g$ estimated from absorption in HCl may be unreliable because of an unknown level of oxidation, assumed to be zero. With forced oxidation, $CaCO_3$ reactivity was estimated to be $2.3\times10^5$ sec/cm$^2$ assuming 30 seconds liquid residence time in the bubbler. With natural oxidation, the $CaCO_3$ reactivity was reduced to $10^5$ sec/cm$^2$ to simulate $SO_2$ removal accurately. This adjustment may reflect a moderate level of limestone blinding. $CaSO_3$ reactivity was also taken to be $10^5$ sec/cm$^2$.

The level of natural oxidation observed in the Radian tests was 40 to 60%. This relatively high level of oxidation may occur in the hold tank or in the scrubber itself. With no hold tank oxidation, an oxidation enhancement factor of 2 to 4 was required to simulate observed levels of

## TABLE 1. EXPERIMENTAL CONDITIONS AND MODEL PARAMETERS

| Scrubber Specification | Radian<br>Bubbler 5.28 cm Liquid Depth | EPA-RTP<br>Turbulent Contactor Absorber, three 18-cm beds, 4-cm spheres | CE<br>Spray Absorber Single Nozzle Level 4 spray levels |
|---|---|---|---|
| Gas Rate ($m^3$/min) | 0.018 | 7.8 | 34 |
| Scrubber Cross Section ($cm^2$) | 11.4 | 410.0 | 3716.0 |
| Gas composition (atm) | | | |
| $SO_2 \times 10^3$ | 2.1 | 0.5; 2.5 | 0.5; 1.5 |
| $CO_2$ | 0.12 | 0.06 | 0.06 |
| $O_2$ | 0.01-0.07 | 0.04-0.08 | 0.05-0.09 |
| Temperature (°C) | 50 | 60 | 60 |
| Number of stages | 1 | 3 | 3 |
| $N_g$ | 2.2 | 6.9 | 1.8 |
| $k_\ell^\circ/k_g$ (atm/M) | 0.9 | 0.2 | 0.4 |
| L/G ($M^{-1}$) | 0.25 | 0.23 | 0.25 |
| E | 2 | 2 | 1,7 |
| $K_{CaCO_3}$ (sec/$cm^2$) | | | |
| Forced Oxidation | $2.3 \times 10^5$ | $6 \times 10^3$, $5 \times 10^4$ | - |
| Natural Oxidation | $10^5$ | $5 \times 10^3$, $10^4$ | 0 |
| $K_{CaSO_3}$ (sec/$cm^2$) | | | |
| Forced Oxidation | 0 | 0 | - |
| Natural Oxidation | $10^5$ | $10^4$ | 0 |
| Limestone Stoichiometry | 1.4 | 1.2-1.4 | 1.48-1.87 |

solid oxidation. This enhancement factor also simulated the observed levels of $SO_2$ removal in most of the experiments with clear solution scrubbing. The results in Figure 2 were calculated with an oxidation enhancement factor of 2.

As shown in Figure 2, the $SO_2$ removal for natural oxidation with NaCl or $CaCl_2$ and forced oxidation with $CaCl_2$ is simulated well by these conditions. However, with NaCl and forced oxidation the model predicts $SO_2$ removal 2 to 10% higher than the experimental values.

EPA-RTP

Simulated results with the 3-stage TCA at EPA's Industrial Environmental Research Laboratory in Research Triangle Park (RTP), N.C., are presented in Figures 3 and 4. The number of gas-phase mass transfer units was estimated to be 6.9 by absorption of $SO_2$ in $Na_2CO_3$ solution. The paramater $k_\ell^\circ/k_g$ was found to be 0.2 atm/M by absorption of $CO_2$ into $Na_2CO_3/NaHCO_3$ solution.[8] An oxidation enhancement factor of 2 was necessary to simulate observed levels of natural oxidation. Assuming 7 seconds liquid residence time in the scrubber, the estimated limestone reactivity was $2x10^4$ sec/cm$^2$ at 1.2 stoichiometry and $4x10^4$ sec/cm$^2$ at 1.4 stoichiometry. An even value of $5x10^4$ sec/cm$^2$ was used to simulate the forced oxidation data at 1.2 stoichiometry.

$SO_2$ removal with forced oxidation and $CaCl_2$ or NaCl was simulated well by this set of parameters with chloride concentration greater than 20,000 ppm (Figure 3). However at low chloride it was necessary to reduce limestone reactivity to $6x10^3$ sec/cm$^2$ in order to simulate $SO_2$ removal. This reduction is consistent with the tendency to get "limestone blinding" in systems with forced oxidation at higher pH.

$SO_2$ removal with natural oxidation was overpredicted with the estimated value of limestone reactivity. With an order-of-magnitude lower reactivity ($10^4$ sec/cm$^2$ at 1.4 stoichiometry and $5x10^3$ sec/cm$^2$ at 1.2 stoichiometry), the $SO_2$ removal is simulated reasonably well over the entire range of chloride concentration (Figure 3). The predicted $SO_2$ removal at low stoichiometry was less than at high stoichiometry primarily because of reduced bicarbonate concentration in the scrubber inlet solution. $CaSO_3$ reactivity had little effect on $SO_2$ removal up to $10^4$ sec/cm$^2$, and that value gave the best fit of $SO_2$ removal over the entire range of chloride.

Figure 4 shows how the model simulates the observed effects of buffer additive at 50,000 ppm chloride and 1.4 limestone stoichiometry. The byproduct dibasic acid (DBA) used in these tests was mostly glutaric acid, but it was modeled by assigning to it the same properties as adipic acid. Assuming 1 mole of DBA as analyzed by the silicic acid method is equivalent to 1 mole adipic acid, Figure 4 shows that the model overpredicts the effect of DBA. However, with 0.65 moles adipic acid/mole DBA, the model predicts accurately the effect of DBA.

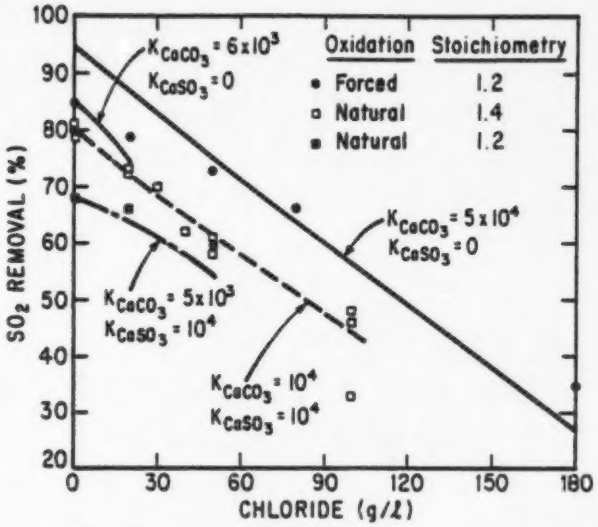

Figure 3. Simulation of EPA-RTP Data on the Effects of $CaCl_2$. Curves Calculated Using Conditions in Table 1.

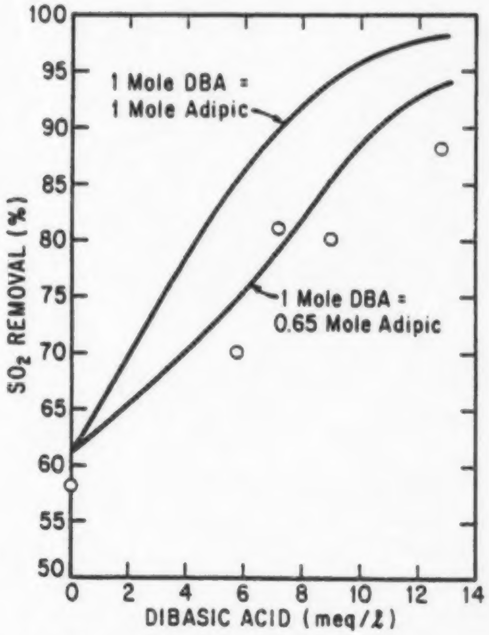

Figure 4. Effect of Dibasic Acid on $SO_2$ Removal with 0.7 M $CaCl_2$, Natural Oxidation, and 1.4 Limestone Stoichiometry (EPA-RTP data), Curve Calculated Using Conditions in Table 1 ($K_{CaCO_3} = K_{CaSO_3} = 10^4$ sec/cm$^2$).

## COMBUSTION ENGINEERING (CE)

The simulation of CE data is given in Figure 5. The CE data were collected in a spray tower with very short liquid-phase residence time. Therefore, the $CaCO_3$ and $CaSO_3$ reactivities were taken to be zero.

The simulated $SO_2$ removal was insensitive to $N_g$ and $k_\ell^\circ/k_g$, but varied significantly with the oxidation enhancement factor, E. $N_g$ and $k_\ell^\circ/k_g$ were arbitrarily set at 1.8 and 0.4 atm/M, respectively. The data were simulated best by E equal to 7, giving a calculated oxidation level near 100%. The observed oxidation level was 60 to 90%, but these were short experiments and the solids oxidation may not have reached steady state. Figure 5 shows that the model simulates $SO_2$ removal at both 500 and 1500 ppm $SO_2$ in the inlet gas.

## DISCUSSION

There are several effects evident from these theoretical and experimental results. When chloride accumulates in scrubber solution, it increases the ionic strength and thereby changes activity coefficients for most solution species. If it shows up with $Ca^{++}$, it can also affect solid/liquid equilibria directly. These chloride effects can interact with the effects of bicarbonate accumulation and sulfite oxidation. The effectiveness of buffer additives is also reduced by the pH effects of $CaCl_2$ accumulation. Limestone blinding does not appear to be caused by chloride accumulation, but does affect interpretation of results with natural oxidation.

## EFFECTS OF IONIC STRENGTH

Chloride salts with any cations affect solution equilibria by changing the ionic strength and resulting activity coefficients. The hydrolysis of $SO_2$ is one of the important equilibrium reactions enhancing $SO_2$ absorption (Chang and Rochelle, 1981):

$$SO_2 + H_2O \rightleftarrows H^+ + HSO_3^-$$

$$K_h = \frac{[H^+][HSO_3^-]}{P_{SO_2}} \qquad (26)$$

The apparent equilibrium constant for this reaction varies substantially with ionic strength as shown in Figure 6. These results include the effects of ion pairs and show somewhat improved equilibrium in $CaCl_2$ and $MgCl_2$ solutions. Figure 2 shows that NaCl accumulation reduces $SO_2$ removal in a manner similar to its impact on $K_h$.

## EFFECTS OF $CA^{++}$ CONCENTRATION

If $Na^+$ or $Mg^{++}$ is available in lower equivalent concentration than $Cl^-$,

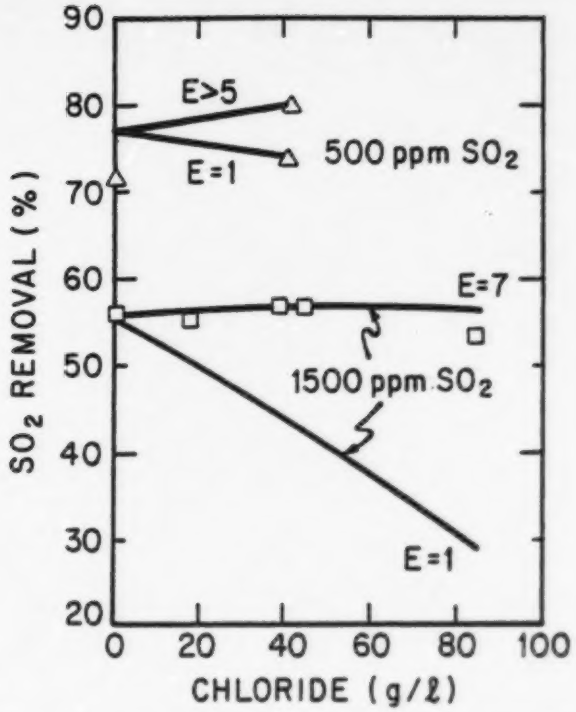

Figure 5. Simulation of CE Data, Curves Calculated Using Conditions in Table 1.

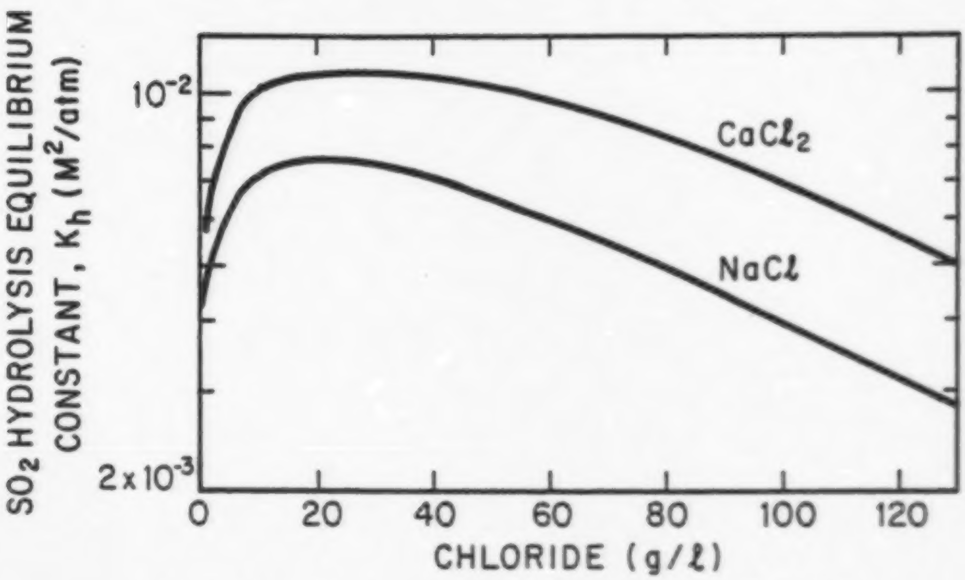

Figure 6. Apparent Equilibrium Constant for $SO_2$ Hydrolysis in $CaCl_2$ and NaCl Solutions.

the chloride will accumulate in solution as $CaCl_2$. $Ca^{++}$ has specific effects on the solid/liquid equilibria and rate processes that determine the pH and concentration of dissolved alkalinity ($HCO_3^-$ and $SO_3^=$) in the scrubber inlet solution and the scrubber itself. $SO_2$ absorption is enhanced by dissolved alkalinity, so $Ca^{++}$ can affect $SO_2$ removal.

The concentrations of $SO_3^=$ and $HCO_3^-$ are controlled by an approach to equilibrium with $CaSO_3$:

$$CaSO_3(s) \rightleftarrows Ca^{++} + SO_3^=$$

$$[SO_3^=] = K_{sp,CaSO_3}/[Ca^{++}] \tag{27}$$

and the equilibrium with calcite:

$$CaCO_3\ (s) + CO_2 + H_2O \rightleftarrows Ca^{++} + 2HCO_3^-$$

$$[HCO_3^-]^2 = K_{calcite}\ \frac{P_{CO_2}}{[Ca^{++}]} \tag{28}$$

Therefore, both $[HCO_3^-]$ and $[SO_3^=]$ should decrease as $[Ca^{++}]$ increases.

Table 2 shows the calculated dissolved alkalinity in the scrubber inlet solution. Typically there is less than 2 mM dissolved alkalinity in experiments using forced oxidation, because $SO_3^=$ is oxidized and $CO_2/HCO_3^-$ is stripped by the sparging air. With natural oxidation the typical level of dissolved alkalinity was 2 mM. The only experiments giving higher levels of dissolved alkalinity were those at EPA-RTP with less than 25 mM $Ca^{++}$ and high limestone stoichiometry (NB-1, 5.2 mM; NN-1, 6.1 mM). The comparable experiments at Radian gave only 3 mM alkalinity, probably because $CO_2$ easily escaped from the small hold tank, giving lower $HCO_3^-$ alkalinity and only 0.06 atm $CO_2$ vapor pressure, compared to 0.25 atm at EPA-RTP. Furthermore, the EPA-RTP experiment at low limestone stoichiometry also gave only 3.7 mM alkalinity with less than 25 mM $Ca^{++}$, because of the low hold tank pH. Therefore only the EPA-RTP experiments with natural oxidation show the strong effects of $CaCl_2$ accumulation on $SO_2$ removal, because of the combined effects on the $SO_2$ hydrolysis reaction and the dissolved alkalinity.

The effect of $Ca^{++}$ on dissolved alkalinity in the scrubber is more difficult to quantify. However, the experiments with forced oxidation show that NaCl accumulation affects $SO_2$ removal less than $CaCl_2$ accumulation, even though there is no significant dissolved alkalinity in the inlet solution in either case. These results are consistent with a specific effect of $Ca^{++}$ on the dissolved alkalinity in the scrubber.

In general high dissolved alkalinity in the absence of chloride is most likely to occur with high pH (high limestone stoichiometry) under conditions

## TABLE 2. HOLD TANK EQUILIBRIA

| Run No. | $Ca^{++}$ (mM) | $Na^{+}$ (mM) | pH | $P^{*}_{CO_2}$ (atm) | Saturation[a] $CaSO_3$ | Saturation[a] $CaCO_3$ | $a^2_{H^+}/[Ca^{++}]$ ($M\times10^{-11}$) | Alkalinity (mM) Total | Alkalinity (mM) $HCO_3^-$ |
|---|---|---|---|---|---|---|---|---|---|
| **EPA-RTP - Natural Oxidation - High Limestone Stoichiometry** | | | | | | | | | |
| NB-1 | 10 | - | 6.0 | 0.28 | 0.9 | 0.6 | 18 | 5.2 | 3.8 |
| N1-1 | 140 | - | 5.5 | 0.18 | 1.0 | 0.6 | 8 | 2.2 | 0.9 |
| N2-1 | 270 | - | 5.3 | 0.20 | 0.8 | 0.5 | 10 | 2.0 | 1.3 |
| N3-1 | 390 | - | 5.2 | 0.22 | 0.9 | 0.5 | 10 | 2.0 | 1.4 |
| N4-1 | 550 | - | 5.1 | 0.24 | 0.9 | 0.5 | 12 | 2.2 | 1.5 |
| N5-1 | 670 | - | 4.9 | 0.19 | 1.7 | 0.2 | 24 | 2.0 | 0.9 |
| N5-9 | 670 | - | 5.1 | 0.16 | 1.1 | 0.5 | 10 | 1.9 | 1.2 |
| N10-1 | 1400 | - | 4.6 | 0.24 | 0.5 | 0.4 | 45 | 1.5 | 1.3 |
| NN-1 | 23 | 710 | 5.9 | 0.28 | 1.3 | 0.8 | 8 | 6.1 | 4.4 |
| NN-3 | 24 | 1420 | 5.9 | 0.18 | 1.3 | 0.6 | 7 | 4.4 | 2.6 |
| NN-2 | 350 | 720 | 5.2 | 0.20 | 1.7 | 0.4 | 12 | 2.4 | 1.2 |
| | | Mg | | | | | | | |
| Mg-6 | 360 | 290 | 5.4 | 0.25 | 1.3 | 1.3 | 5 | 6.3 | 1.7 |
| Mg-7 | 46 | 580 | 5.1 | 0.30 | 1.6 | 1.0 | 11 | 8.6 | 1.5 |
| Mg-8 | 280 | 290 | 5.1 | 0.22 | 0.7 | 0.6 | 11 | 1.9 | 1.2 |
| **EPA-RTP - Natural Oxidation - Low Limestone Stoichiometry** | | | | | | | | | |
| | | $Na^{+}$ | | | | | | | |
| LS-B | 24 | - | 5.6 | 0.18 | 2.1 | 0.4 | 45 | 3.7 | 1.1 |
| LS-2 | 280 | - | 4.9 | 0.18 | 1.0 | 0.07 | 59 | 1.3 | 0.5 |
| LS-5 | 680 | - | 4.6 | 0.17 | 0.8 | 0.05 | 93 | 0.9 | 0.4 |
| **Radian - Natural Oxidation - High Stoichiometry** | | | | | | | | | |
| TDS-13 | 20 | - | 6.3 | 0.08 | 1.2 | 1.8 | 1.8 | 3.6 | 2.3 |
| TDS-19 | 20 | - | 6.2 | 0.08 | 1.0 | 0.9 | 3.6 | 2.7 | 1.6 |
| TDS-18 | 20 | - | 6.3 | 0.06 | 1.1 | 1.3 | 1.9 | 2.7 | 1.6 |
| TDS-13 | 1880 | - | 4.9 | 0.06 | 0.7 | 0.9 | 8 | 1.2 | 0.9 |
| TDS-19 | 2160 | - | 4.9 | 0.05 | - | 0.9 | 9 | - | 0.7 |
| TDS-18 | 62 | 4330 | 5.8 | 0.07 | 1.4 | 0.6 | 8 | 1.6 | 0.8 |
| **EPA-RTP - Forced Oxidation** | | | | | | | | | |
| FB-1 | 16 | - | 6.6 | 0.04 | 0.01 | 2.0 | 0.7 | 2.3 | 2.3 |
| FB-2 | 12 | - | 7.1 | 0.01 | 0.06 | 3.4 | 0.1 | 1.9 | 1.8 |
| F5-1 | 672 | - | 5.7 | 0.03 | 0.06 | 0.1 | 0.6 | 0.1 | 0.08 |
| F8-1 | 1130 | - | 5.5 | 0.05 | 0.2 | 2.8 | 0.9 | 1.7 | 1.6 |
| FN-5 | 29 | 3130 | 5.6 | 0.02 | 0 | 0.06 | 23 | 0.2 | 0.2 |
| FN-3 | 28 | 2340 | 5.8 | 0.01 | 0 | 0.05 | 10 | 0.3 | 0.3 |
| **Radian - Forced Oxidation** | | | | | | | | | |
| TDS-14 | 18 | - | 6.7 | 0.02 | - | 2.6 | 0.4 | 1.4 | 1.4 |
| TDS-17 | 18 | - | 6.7 | 0.02 | 0.08 | 2.2 | 0.4 | 1.2 | 1.2 |
| TDS-14 | 2370 | - | 5.4 | 0.01 | 0 | 3.3 | 0.9 | 0.6 | 0.6 |
| TDS-17 | 27 | 4270 | 6.2 | 0.01 | 0.06 | 6.1 | 0.1 | 0.6 | 0.6 |

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[a] $CaSO_3$ Saturation $= a_{Ca^{++}}\, a_{SO_3^{=}}/2.6\times10^{-7}$, $CaCO_3$ Saturation $= a_{Ca^{++}}\, a_{CO_3^{=}}/8.6\times10^{-10}$

where $CO_2$ is not lost from the hold tank. High dissolved alkalinity can also result from excess $Na^+$ or $Mg^{++}$ in the scrubber system. With either of these conditions there can be a dramatic decrease in $SO_2$ removal if an accumulation of chloride causes $Ca^{++}$ concentration to increase from less than 25 mM to more than 100 mM.

Table 2 gives calculated thermodynamic parameters for EPA-RTP and Radian scrubber inlet solutions. With natural oxidation, the scrubber inlet solution is essentially saturated to $CaSO_3$, with calculated $CaSO_3$ saturations varying from 0.7 to 1.7. With high limestone stoichiometry (1.4) and natural oxidation, the $CaCO_3$ saturation of the scrubber inlet solution is also nearly constant. It varies from 0.4 to 0.8 based on calcite solubility. The calculated vapor pressure of $CO_2$ varies from 0.18 to 0.28 atm and is also approximately constant. To the extent that $CaCO_3$ saturation and the $CO_2$ vapor pressure are constant, pH is given approximately by the equilibrium:

$$CaCO_3 + 2H^+ \rightleftarrows Ca^{++} + CO_2 \qquad a^2_{H^+} = K\,P^*_{CO_2}/[Ca^{++}] \qquad (29)$$

As shown in Table 2, the ratio, $a^2_{H^+}/[Ca^{++}]$ varies from $5 \times 10^{-11}$ to $2.6 \times 10^{-10}$ in EPA-RTP experiments at high limestone stoichiometry with natural oxidation and $CaCl_2$ or NaCl.

Table 2 includes data calculated from three runs with $MgCl_2$ at EPA-RTP. It appears that $Mg^{++}$ has the same effect as $Ca^{++}$ on the driving force for limestone dissolution. The values of $CaCO_3$ saturation and $a^2_{H^+}/[Ca^{++}]$ were calculated by substituting $[(a_{Ca^{++}}) + (a_{Mg^{++}})]$ and $[Ca^{++}] + [Mg^{++}]$ for $a_{Ca^{++}}$ and $[Ca^{++}]$, respectively. With this adjustment $CaCO_3$ saturation and $a^2_{H^+}/[Ca^{++}]$ are in the same range as runs with $CaCl_2$.

BUFFER ADDITIVES

Additives such as adipic acid enhance $SO_2$ removal with or without high chlorides by buffering between the inlet and outlet pH of the scrubber, or between the bulk solution pH and the pH at the gas/liquid interface. Because $Ca^{++}$ depresses scrubber inlet pH and bulk solution pH, a larger concentration of adipic acid (or DBA) is required to provide equivalent buffer capacity and $SO_2$ removal with an accumulation of $CaCl_2$. However, as shown in Figure 4, DBA is still effective in enhancing $SO_2$ removal.

LIMESTONE REACTIVITY

Forced oxidation was observed to enhance $SO_2$ removal by 3 to 12% in the EPA-RTP data, 3 to 7% in the Radian data, and hardly at all in the Shawnee data. These observations have no major impact on the interpretation of the chloride effects, but pose some difficult questions about the understanding of general scrubber performance. From the EPA-RTP data, it would appear that limestone reactivity is substantially depressed with natural oxidation, since the $SO_2$ removal with natural oxidation is best simulated by reducing the limestone reactivity a factor of 10 to $3 \times 10^5$. The Radian data show less of an effect, requiring a reduction of a factor of 2, but were collected in a contactor with a liquid-phase residence time three times greater than in the EPA-RTP TCA scrubber. The Shawnee data were collected at 1.1 limestone stoichiometry, where limestone reactivity with natural oxidation is negligible in any case, so forced oxidation would not be expected to enhance $SO_2$ removal.

## SCRUBBER OXIDATION

In all cases an oxidation enhancement factor of 2 to 7 was required to simulate the observed levels of scrubber oxidation. This means that $O_2$ absorption in the scrubber must be enhanced by its fast reaction with dissolved $SO_2$ species in the liquid-phase boundary layer. This reaction is probably catalyzed by Fe and/or Mn (Ulrich, 1983; Ulrich et al., 1983).

The calculated results for the CE experiments demonstrate that levels of scrubber oxidation near 100% can substantially enhance $SO_2$ removal and may cancel out the effects of chloride accumulation. High scrubber oxidation serves to reduce total dissolved sulfite in the scrubber outlet solution and permit satisfactory $SO_2$ removal at lower scrubber outlet pH.

## CONCLUSIONS

1. The integrated scrubber model is able to predict relative effects of NaCl, $CaCl_2$, and dibasic acid on $SO_2$ removal.

2. Chloride accumulation reduces $SO_2$ removal by reducing the apparent equilibrium constant for $SO_2$ hydrolysis.

3. $Ca^{++}$ accumulation reduces $SO_2$ removal by reducing the concentration of $HCO_3^-$ and $SO_3^=$. The effect of $CaCl_2$ accumulation on $SO_2$ removal is greatest in systems that start with a high level of $HCO_3^-$ and $SO_3^=$. The $HCO_3^-$ concentration can depend on $CO_2$ loss from the hold tank.

4. Scrubber oxidation approaching 100% can have a significant impact on $SO_2$ removal.

5. Oxygen absorption in typical scrubbers is 2 to 7 times faster than simple physical absorption because of fast reaction with dissolved $SO_2$.

6. Limestone reactivity in the scrubber can be lower in systems with natural oxidation than in systems with forced oxidation.

## ACKNOWLEDGEMENTS

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# NOTATION

$a_j$ - activity of species j
$a$ - interfacial area, $cm^2/cm^3$
$A$ - solids surface area per volume solution, $cm^2/cm^3$
$C_s$ - concentration of calcium solids in feed, M
$D$ - diffusivity, $cm^2/sec$
$E$ - oxidation enhancement factor
Flux - Flux, $gmol/cm^2$-sec
$G$ - gas flow rate, $gmol/sec\text{-}cm^2$
$H$ - Henry's Law constant, M/atm
$I$ - ionic strength, M
$j$ - general solution or solid species
$K$ - equilibrium constant
$K_{CaCO_3}$ - limestone reactivity, $sec/cm^2$
$K_{CaSO_3}$ - calcium sulfite reactivity, $sec/cm^2$
$K_{sp,j}$ - solubility product for solid j, $M^2$
$k_g$ - gas-phase mass transfer coefficient, $gmol/sec\text{-}cm^2\text{-}atm$
$k^{o}_{\ell}$ - liquid-phase mass transfer coefficient, $liter/sec\text{-}cm^2$
$L$ - liquid flow rate, $liter/sec\text{-}cm^2$
$M$ - molarity, gmol/liter
$N_g$ - number of gas phase transfer units - $k_g a ZP_T/G$
$P$ - partial pressure, atm
$P_T$ - total pressure, atm
pH - negative logarithm of $H^+$ activity
$T$ - liquid holdup, $sec/N_g$
$t$ - residence time of solid particle in scrubber, sec
$U$ - utilization of limestone
$Z$ - height of scrubber, cm
$\delta$ - film thickness, cm
$\Delta$ - difference between bulk and interface or bulk and surface quantities
[ ] - concentration, M

Superscripts:

° - ion pair, degrees

Subscripts:

i - interface (gas/liquid)
b - bulk
s - surface of solid
in - inlet to scrubber
out - outlet of scrubber
T - total quantity of a component

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# INFLUENCE OF HIGH DISSOLVED SOLIDS ON PRECIPITATION KINETICS AND SOLID PARTICLE SIZE

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## ABSTRACT

This paper presents results of a study to screen the effects of high concentrations of dissolved ions on the precipitation of calcium sulfate dihydrate, gypsum, and the solid solution of sulfate with calcium sulfite hemihydrate. A series of precipitation measurements were conducted in the presence of combinations of magnesium, sodium, calcium, chloride, and sulfate at total dissolved solids levels up to 240,000 mg/L.

Significant differences in the precipitation rates and habit and size of the precipitated solids were observed for several of the test solutions as compared to precipitation from dilute solutions. Gypsum precipitation rate in high TDS solutions was accelerated in high TDS solutions, especially those containing chloride ion. The calcium sulfite-sulfate hemihydrate solid solution precipitation rate was faster in sulfate ion solutions.

These results suggest that the operation of FGD systems at high dissolved solids concentrations can alter the precipitation kinetics. Attempts to model these effects will require the incorporation of the concentrations of specific ions in the kinetic relationships.

## INTRODUCTION

Sulfur dioxide ($SO_2$) is removed from flue gases of coal fired power plants by a variety of commercial processes. At present, the lime and limestone flue gas desulfurization (FGD) processes are the most advanced of the throw away FGD systems (1,2,3). These systems remove $SO_2$ from flue gas and convert it to calcium sulfite and calcium sulfate sludge. A calcium sulfite-calcium sulfate sludge is usually produced in natural oxidation systems, while forced oxidation systems produce primarily calcium sulfate sludges.

The chemical reaction kinetics which produce these solids and the solids' respective physical characteristics are especially important in designing and operating FGD systems. The rate at which calcium sulfite and calcium sulfate precipitate is important in controlling scaling on scrubber surfaces and in designing rection tanks (4,5). Also, precipitation rates are important in determining the particle size distribution of the respective sulfur sludge. Particle size distribution has been shown to be a major factor affecting the settling and dewatering properties of calcium sulfite and calcium sulfate sludges. The poor dewatering properties of calcium sulfite and, to a lesser extent, calcium sulfate are well documented and are responsible for most of the problems associated with sludge disposal in FGD systems.

Recently, more emphasis has been placed on water conservation and multiple water usage in power plant design and operation. As a result, it is becoming more common for makeup water to the FGD system to come from such sources as cooling tower blowdown, and other power plant wastewater streams. This operating approach has increased the total dissolved solids (TDS) in some FGD liquors to levels greater than 100,000 mg/L. The increased concentration of total dissolved solids in the FGD system has raised technical questions concerning the application of design and operating criteria for FGD systems gathered at low TDS levels to these new high TDS operating systems. Especially, it has not been determined what effects TDS has upon the precipitation kinetics of calcium sulfite and calcium sulfate. A major difference in precipitation rate may have a damaging effect (causing severe scaling) or it could be beneficial (smaller reaction tank design) to the system design. In addition, there is a need to determine whether the chemical composition associated with high TDS scrubber liquors influences the size and shape of calcium sulfite and sulfate crystals precipitating from these high TDS solutions.

This paper presents the results from a laboratory study funded by the Electric Power Research Institute to screen a broad range of high TDS solutions to determine the relative effect of each solution on the crystallization of calcium sulfate and calcium sulfite. The laboratory study focused on determining the effect of high TDS solutions on the precipitation rate and the crystal size and habit of each calcium-sulfur salt. These results are presented in the following text.

## PRECIPITATION OF GYPSUM IN HIGH TDS SOLUTIONS

The experimental approach used to study the precipitation of gypsum in high TDS solutions, followed by a discussion of the results of these studies is presented in the following paragraphs.

### EXPERIMENTAL APPROACH

A mixed suspension mixed product removal reactor (MSMPR) was used to study the effect of high TDS solutions on gypsum precipitation kinetics and crystal habit and size modification. Figure 1 shows a diagram of the 2-liter MSMPR reactor. The reactor was constructed from Plexiglas and incorporates

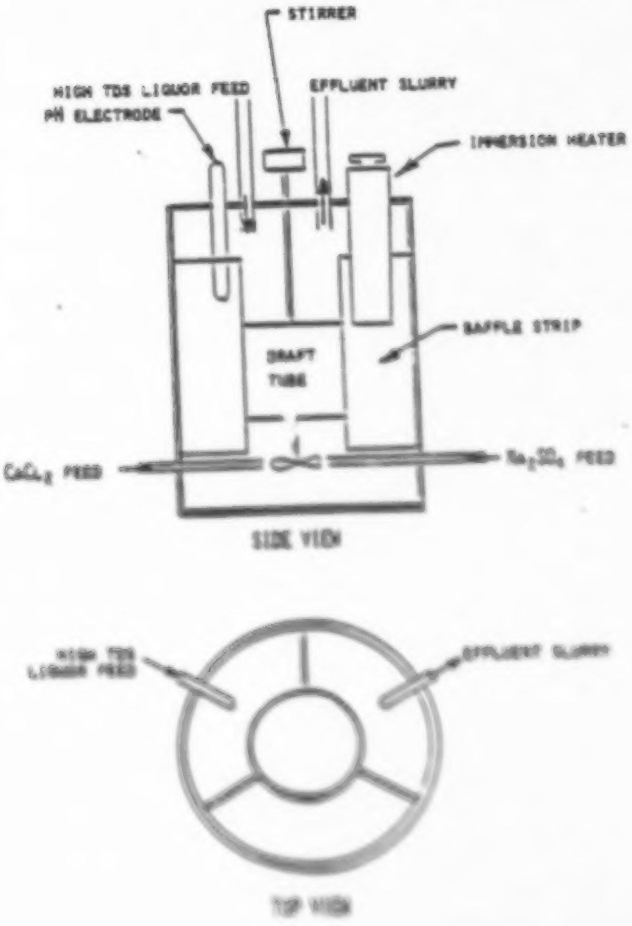


Figure 1. Mixed Suspension-Mixed Product Removal Reactor

a central draft tube with three radial baffle strips. This design, coupled with a single shaft propeller type stirrer mounted along the axis of the draft tube insured a well mixed slurry. The reactor temperature was maintained by an immersion heater controlled by using a thermocouple probe inserted in the reactor. Figure 2 shows the schematic diagram of the experimental setup used in the high TDS tests.

Reagent grade chemicals were used to prepare the feed stocks for all of the crystallizer experiments. The chemical compositions of the high TDS solutions used in the study are shown in Table 1.

The crystallizer slurry was sampled directly from the drawdown stream by rapidly filtering a known volume through a .45* Millipore* membrane filter. The filtrate was diluted with deionized water to prevent additional precipitation and saved for chemical analysis. The solids collected on the filter were rinsed, dryed and weighed to determine the weight percent solids of the slurry according to the following equation:

$$\text{Wt\% Solid} = \frac{\text{Weight Solid}}{\text{Volume of Slurry}} \times 100 \qquad (1)$$

TABLE 1. GYPSU CRYSTALLIZATION--HIGH TDS SOLUTIONS TESTED

| Solution Identification | Chemical Analysis (mg/L) | | | | |
|---|---|---|---|---|---|
| | $Ca^+$ | $Mg^{++}$ | $Na^+$ | $SO_4$ | $Cl^-$ |
| 240K Mix | — | 39,200 | 23,200 | 104,000 | 68,800 |
| 120K Mix | — | 20,700 | 12,200 | 49,700 | 37,700 |
| 30K Mix | — | 4500 | 2700 | 13,300 | 7800 |
| 200K $CaCl_2$ | 72,00 | — | — | — | 127,900 |
| 230K $MgCl_2$ | — | 63,200 | — | — | 186,800 |
| 230K NaCl | — | — | 101,000 | — | 156,000 |
| 230K $Na_2SO_4$ | — | — | 78,200 | 165,000 | — |
| 200K $MgSO_4$ | — | 41,300 | — | 165,000 | — |

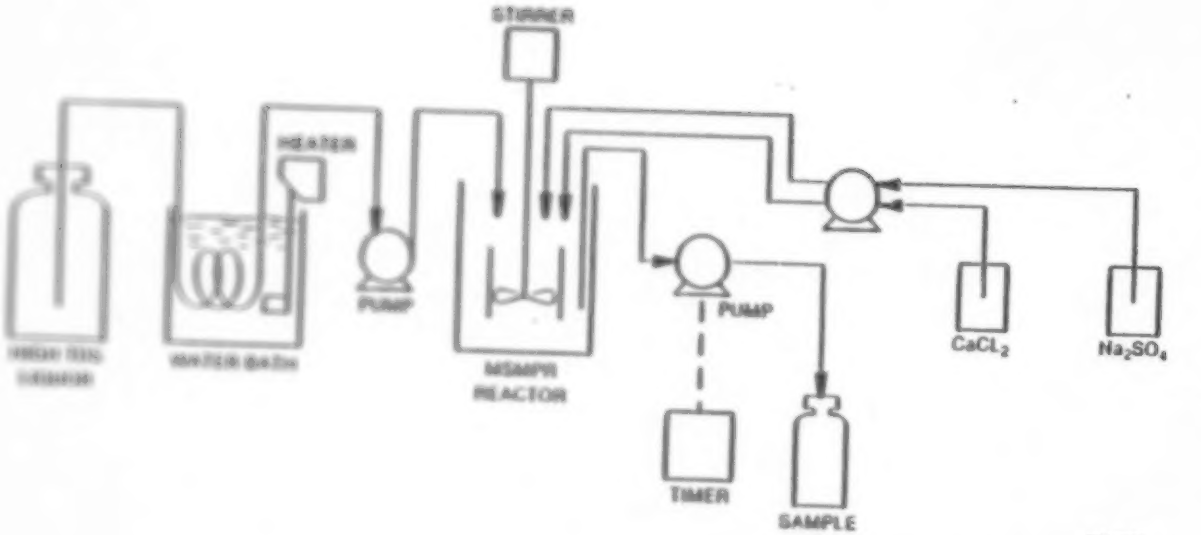


Figure 2. Calcium Sulfate MSMPR Precipitation Rate Experimental Apparatus.

The actual sampling was started after five slurry residence times to monitor the approach to steady state. The crystallizer was operated and samples taken for at least 8-10 residence times for each test. Each test was continued until steady state operation was reached and the sampling was completed. Photomicrographs of selected solid samples were taken for particle size analysis. The characteristic dimension measured was the longest axis of a particular crystal. A typical plot of particle number as a function of size is shown in Figure 3. The linear growth rate of the crystals grown in the MSMPR reactor was determined from the slope of a best-fit line. A detailed description of this techinque of measuring crystal growth rates in the MSMPR reactor is presented elsewhere by Randolph and Larson (6).

The precipitation rate, $P_r$, for each experiment was calculated by Equation 2 which can be derived from a material balance expression:

$$P_r = ([X_i] - [X_f])Q/M_s$$

where $P_r$ = reaction rate of Ca or $SO_4$, mmole/g min L

$[X_i]$ = initial concentration of Ca or $SO_4$, mmole/L

$[X_f]$ = final reactor effluent concentration of Ca or $SO_4$, mmole/L

$Q$ = steady state reactor flow rate, L/min.

$M_s$ = mass of solids in reactor, g

The gypsum precipitation, nucleation, and crystal growth rates are all functions of the relative saturation of $CaSO_4 \cdot 2H_2O$. The relative saturation of gypsum is defined as:

$$\text{Relative Saturation (RS)} = \frac{a_{Ca}\, a_{SO_4}\, a^2_{H_2O}}{K_{sp}} \tag{3}$$

where $a_{Ca}$ = activity of calcium ion

$a_{SO_4}$ = activity of sulfate ion

$a_{H_2O}$ = activity of water

$K_{sp}$ = solubility product of $CaSO_4 \cdot 2H_2O$

The high TDS solutions used in this study required a more empirical approach to measure gypsum relative saturations since ion activities could not be calculated accurately. The gypsum relative saturation or supersaturation was calculated as follows:

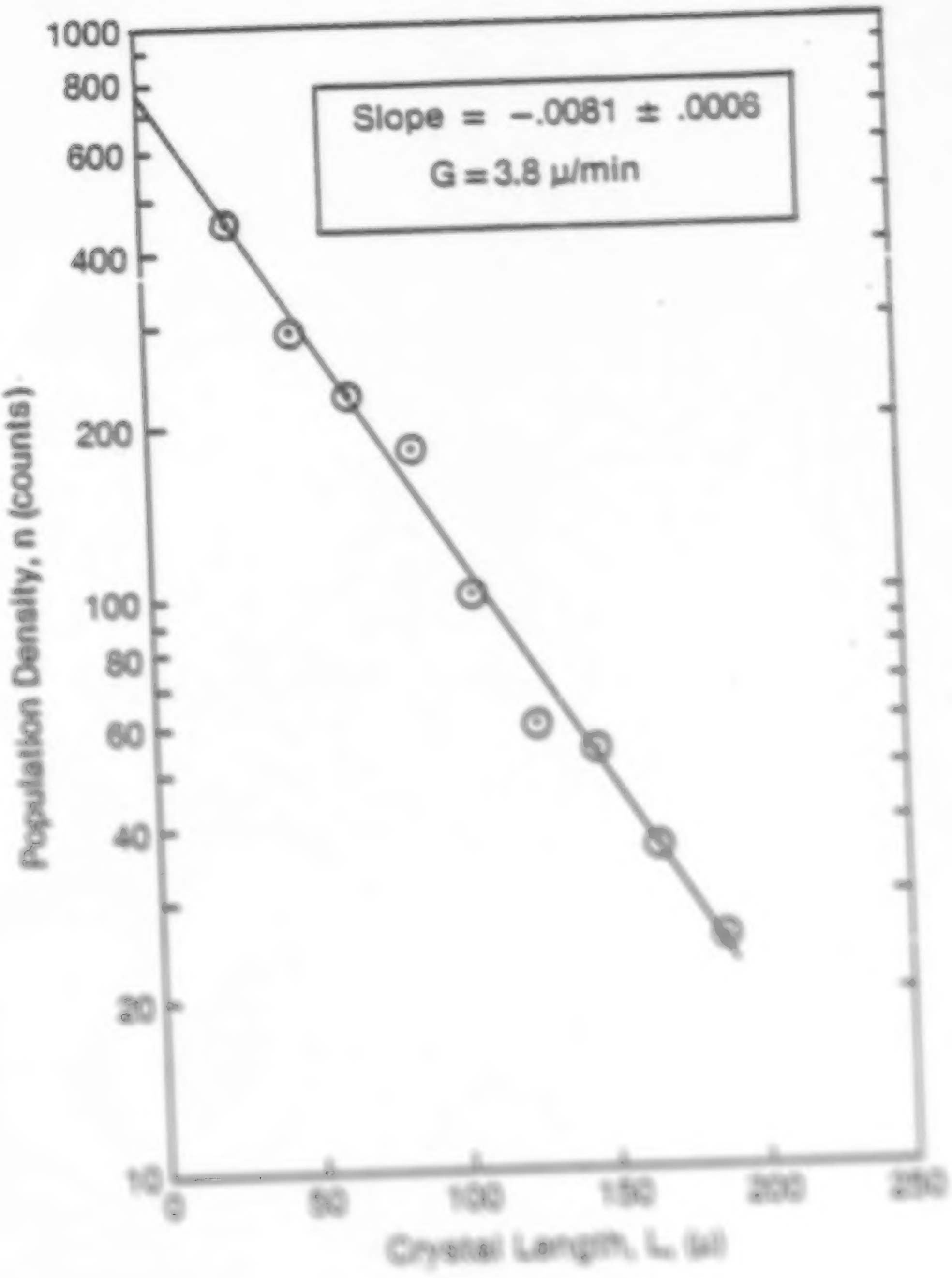


Figure 3. Typical crystal size distribution of $CaSO_4 \cdot 2H_2O$

$$RS_{CaSO_4 \cdot 2H_2O} = \frac{[Ca^{++}]_{ss}\ [SO_4^{=}]_{ss}}{[Ca^{++}]_{eq}\ [SO_4^{=}]_{eq}} \qquad (4)$$

where $[Ca^{++}]_{ss}$ = reactor steady state calcium concentration, mmole/l

$[CA^{++}]_{eq}$ = calcium concentration in equilibrated slurry, mmole/l

$[SO_4^{=}]_{ss}$ = sulfate steady-state sulfate concentration, mmole/l

$[SO_4^{=}]_{eq}$ = sulfate concentration in equilibrated slurry, mmole/l

When [Ca] is much less than $[SO_4]$ in the high TDS liquor, Equation (4) can be reduced to:

$$RS_{CaSO_4 \cdot 2H_2O} = \frac{[Ca^{++}_{ss}]}{[Ca^{++}_{eq}]} \qquad (5)$$

Depending upon the solution conditions, Equations (4) and (5) were used to calculate the gypsum relative saturation in each precipitation rate test. The steady-state calcium and sulfate concentrations were determined for each test. The respective equilibration concentrations were determined by equilibrating slurry samples for a 2-3 week period at 50°C.

## GYPSUM PRECIPITATION IN HIGH TDS SOLUTIONS STUDY RESULTS

The experimental results for the gypsum precipitation rate tests in high TDS solutions are summarized in Table 2. A plot of precipitation rate versus calcium sulfate supersaturation for all of the 240K tests is shown in Figure 4. Three distinct bands of data (I, II, III) are shown. Data band I corresponds to the NaCl and $MgCl_2$ solutions. Data band II represents the $Na_2SO_4$, $MgSO_4$, and mixed liquor compositions, while data band III shows the $CaCl_2$ data. The precipitation rate for a given relative saturation in the NaCl, and $MgCl_2$ test liquors was found to be between 2-3 times greater than the rate measured in the $MgSO_4$, $Na_2SO_4$, and mixed liquors. The third data band (III) shown in Figure 4 represents the 240K $CaCl_2$ solution tests. Note the high supersaturation levels achieved during these runs. However, the corresponding precipitation rates were much lower than would be expected by extrapolating results of the other conditions to these

## Table 2.
## EXPERIMENTAL RESULTS--PRECIPITATION OF $CaSO_4 \cdot 2H_2O$ IN HIGH TDS LIQUORS

| | | Calcium Material Balance | | | Reactor Conditions | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Run No. | Scrubber Liquor (TDS) | Feed $mmole \cdot min^{-1}$ | Effluent $mmole \cdot min^{-1}$ | Delta $mmole \cdot min^{-1}$ | Temp. (°C) | pH | Stirrer Speed (rpm) | Gypsum RS | Precipitation Rate $(mmole \cdot g^{-1} \cdot min^{-1})$ |
| 1 | Mixed 28K | 2.19 | 1.65 | 0.54 | 50 | 4.80 | 900 | 1.63 | 0.74 |
| 2 | Mixed 28K | 1.88 | 1.54 | 0.34 | 50 | 4.35 | 900 | 1.54 | 0.70 |
| 3 | Mixed 28K | 1.93 | 1.58 | 0.35 | 50 | 4.45 | 900 | 1.60 | 0.61 |
| 4 | Mixed 120K | 3.39 | 2.28 | 1.11 | 50 | 6.05 | 900 | 1.41 | 0.61 |
| 5 | Mixed 120K | 3.78 | 2.21 | 1.57 | 50 | 6.20 | 900 | 1.40 | 0.72 |
| 6 | Mixed 120K | 3.12 | 2.34 | 0.78 | 50 | 6.15 | 900 | 1.46 | 1.19 |
| 7 | Mixed 235K | 2.05 | 1.49 | 0.56 | 50 | 6.25 | 900 | 1.41 | 0.85 |
| 8 | Mixed 235K | 2.62 | 1.42 | 1.20 | 50 | 6.30 | 900 | 1.35 | 0.79 |
| 9 | Mixed 110K | 3.28 | 1.41 | 1.87 | 50 | 6.18 | 900 | 1.34 | 0.79 |
| 10 | Mixed 110K | 3.00 | 1.24 | 1.76 | 50 | 5.95 | 900 | 1.36 | 0.63 |
| 11 | Mixed 110K | 1.74 | 1.27 | 0.47 | 50 | 6.25 | 900 | 1.40 | 0.72 |
| 12 | Mixed 110K | 5.61 | 1.33 | 4.28 | 50 | 6.40 | 900 | 1.35 | 0.63 |
| 13 | Mixed 110K | 1.36 | 0.63 | 0.74 | 50 | 6.28 | 900 | 1.32 | 0.38 |
| 14 | Mixed 110K | 1.37 | 0.78 | 0.59 | 50 | 6.22 | 900 | 1.20 | 0.46 |
| 15 | Mixed 110K | 0.91 | 0.88 | 0.09 | 50 | 5.95 | 900 | 1.26 | 0.25 |
| 16 | Mixed 110K | 1.41 | 0.78 | 0.38 | 50 | 6.32 | 900 | 1.22 | 0.38 |
| 17 | Mixed 110K | 2.05 | 1.49 | 0.56 | 50 | 6.15 | 900 | 1.41 | 0.85 |
| 18 | Mixed 110K | 2.62 | 1.42 | 1.20 | 50 | 6.38 | 900 | 1.35 | 0.79 |
| 19 | Mixed 110K | 3.28 | 1.41 | 1.87 | 50 | 6.40 | 900 | 1.34 | 0.79 |
| 20 | $CaCl_2$ 192K | 1.19 | 0.74 | 0.45 | 50 | 5.60 | 900 | 2.00[†] | 1.74 |
| 21 | $CaCl_2$ 192K | 1.63 | 0.72 | 0.91 | 50 | 5.45 | 900 | 2.20[†] | 1.38 |
| 22 | $CaCl_2$ 192K | 1.64 | 0.74 | 0.90 | 50 | 5.22 | 900 | 2.36[†] | 1.96 |
| 23 | NaCl 257K | 7.98 | 5.33 | 2.65 | 50 | 3.50 | 900 | 1.19 | 1.02 |
| 24 | NaCl 257K | 7.35 | 5.77 | 1.58 | 50 | 3.48 | 900 | 1.28 | 1.50 |
| 25 | NaCl 257K | 8.10 | 5.65 | 2.45 | 50 | 3.55 | 900 | 1.24 | 1.23 |
| 26 | NaCl 257K | 3.75 | 2.52 | 1.23 | 50 | 3.50 | 900 | 1.07 | 0.40 |
| 27 | $MgCl_2$ 255K | 911 | 7.61 | 1.49 | 50 | 3.80 | 900 | 1.35 | 1.34 |
| 28 | $MgCl_2$ 255K | 8.31 | 6.55 | 1.76 | 50 | 4.10 | 900 | 1.25 | 0.79 |
| 29 | $MgCl_2$ 255K | 9.83 | 6.26 | 3.57 | 50 | 3.90 | 900 | 1.20 | 0.92 |
| 30 | $Na_2SO_4$ 243K | 3.83 | 2.54 | 1.29 | 50 | 6.40 | 900 | 1.47 | 0.94 |
| 31 | $Na_2SO_4$ 243K | 3.39 | 2.57 | 0.82 | 50 | 6.32 | 900 | 1.46 | 0.86 |
| 32 | $Na_2SO_4$ 243K | 4.27 | 2.49 | 1.78 | 50 | 6.25 | 900 | 1.43 | 0.74 |
| 33 | $Na_2SO_4$ 243K | 3.52 | 0.97 | 2.56 | 50 | 6.45 | 900 | 1.20 | 0.13 |
| 34 | $Na_2SO_4$ 243K | 3.23 | 2.36 | 0.87 | 50 | 6.10 | 900 | 1.41 | 0.46 |
| 35 | $MgSO_4$ 206K | 3.27 | 1.80 | 1.47 | 50 | 6.80 | 900 | 1.38 | 0.69 |
| 36 | $MgSO_4$ 206K | 2.73 | 1.84 | 0.89 | 50 | 6.75 | 900 | 1.42 | 0.71 |
| 37 | $MgSO_4$ 206K | 2.25 | 1.80 | 0.45 | 50 | 6.82 | 900 | 1.36 | 1.01 |
| 38 | Dilute Solution | 5.78 | 3.66 | 2.12 | 50 | 5.50 | 900 | 1.56 | 0187 |

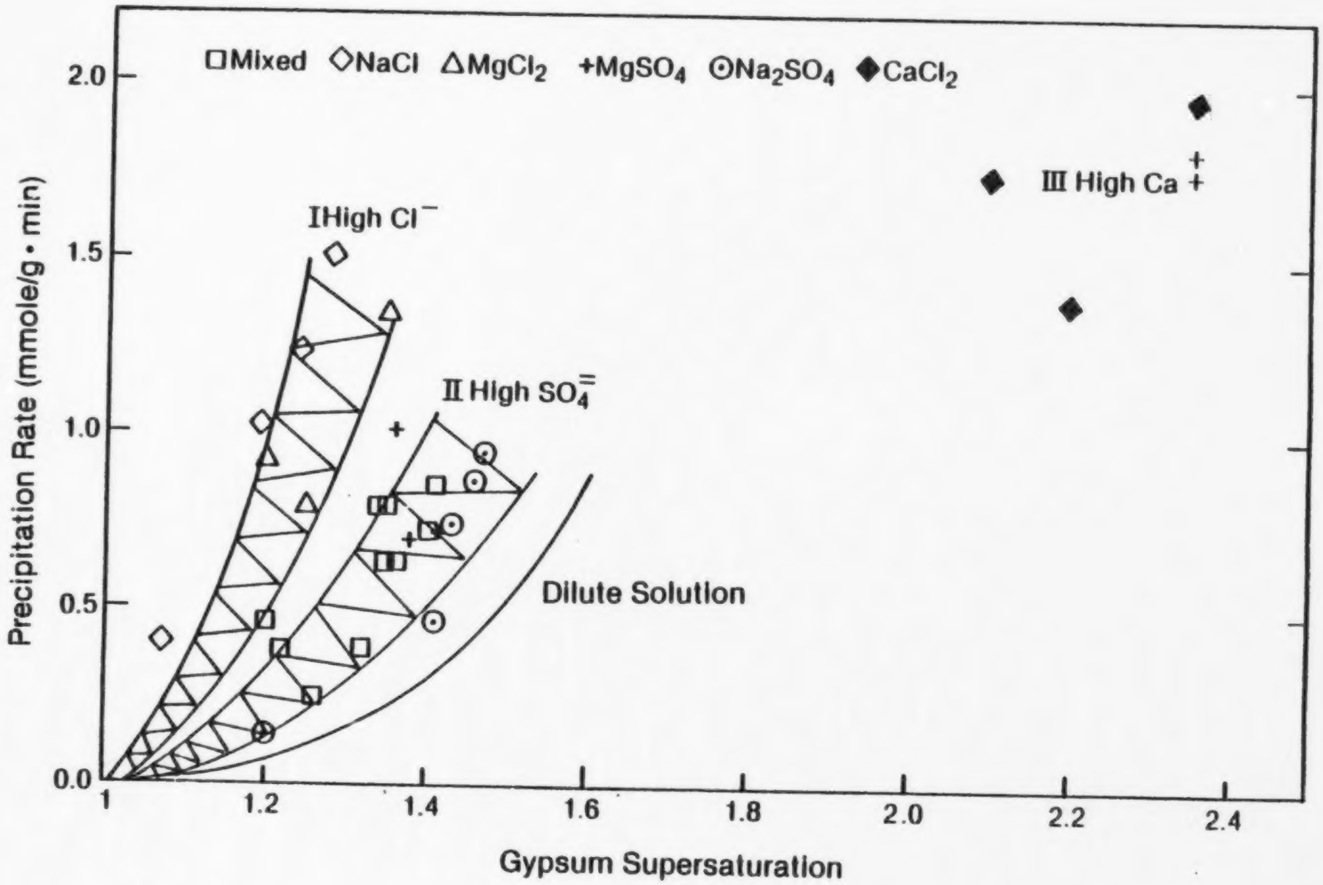


Figure 4. Gypsum Precipitation Rate versus Supersaturation for all 240K High TDS Tests.

same high supersaturations. This may be explained by the fact that in the presence of high calcium concentrations the sulfate concentrations are significantly reduced and can thus become diffusion rate limited.

The level of total dissolved solids (TDS) in actual scrubber liquors is expected to increase as FGD systems switch to makeup waters such as cooling tower blowdown. From a design and operations standpoint it is especially important to know what the effect of increasing the TDS in a scrubber liquor will have on the calcium sulfate precipitation rate. The mixed solution consisting of Na, Mg, Cl, and $SO_4$ was tested at 3 TDS values (30,000 mg/l, 120,000 mg/l, 240,000). The overall precipitation rate was found to increase as the TDS level was raised from 30,000 mg/l to 240,000 mg/l. Further data analysis showed that the increase in precipitation rate was primarily a result of increase in crystal growth as opposed to nucleation. The effect of TDS level on the enhanced gypsum growth rate in the mixed liquor solution is shown in Figure 5. The differences in relative saturation among the TDS levels was accounted for qualitatively.

## HIGH TDS EFFECTS ON GYPSUM SIZE AND HABIT

Changes in crystal habit and size are important in determining the physical properties of crystal slurries. The settling and dewatering characteristics of gypsum sludge produced in the flue gas desulfurization process are of special interest to the design and operating engineer. The effect of high TDS levels on gypsum crystal habit and size was previously unknown. The following paragraphs report the results obtained by this study on the effect of liquor chemical composition on gypsum crystal size and habit.

Table 3 lists the high TDS liquor solution compositions along with the observed crystal habit and the gypsum relative saturation at which the crystals were grown. A key showing the different shapes of the monoclinic gypsum system appears at the bottom of the table. Scanning electron photomicrographs were taken of each test solution solids and are shown in Figures 6 and 7. Each photomicrograph was taken at about 200X magnification and a micrometer scale is shown between the arrows of each photomicrograph for reference.

Gypsum precipitation in dilute solution (Figures 6a and 7a) exhibited agglomerate crystal structures reflective of the high relative saturation growth conditions. $MgCl_2$, $MgSO_4$, and the mixed high TDS liquors all produced very needle-like (acicular) crystals (Figures 6a, 7c and 7d). Alternatively, the NaCl and $Na_2SO_4$ solutions produced gypsum crystals more columnar in habit as shown in Figure 6b and 7b, respectively. The $CaCl_2$ liquor had the most dramatic effect on gypsum crystal habit modification. Figure 6c shows the $CaCl_2$ solutions gypsum crystals grown at comparably higher relative saturations, RS=2.2. These gypsum crystals were

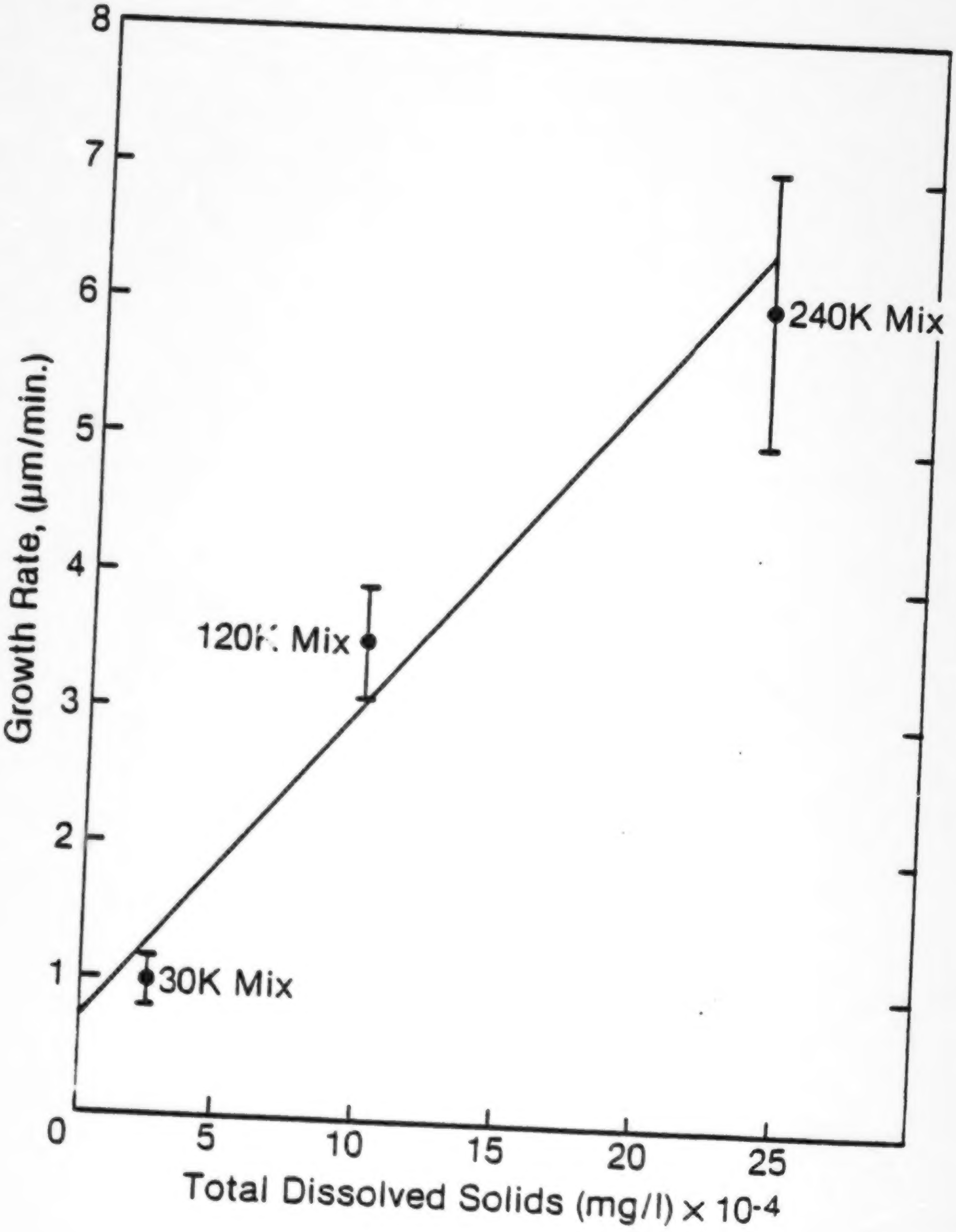
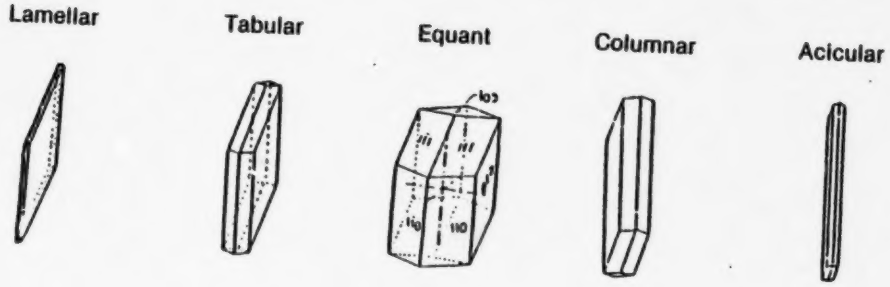


Figure 5. Growth rate vs TDS level for mixed liquor solutions.

Table 3.

## Gypsum Crystal Habit in High TDS Liquor Solutions

| Solution Identification in mg/l | $CaSO_4 . 2H_2O$ Crystal Habit | $CaSO_4 . 2H_2O$ Relative Saturation |
|---|---|---|
| Dilute Solution (Base Case) | Agglomerate | 1.55 |
| 250K NaCl | Agglomerate/Columnar | 1.30 |
| 250K $MgCl_2$ | Acicular | 1.25 |
| 200K $CaCl_2$ | Lamellar | 2.20 |
| 250K $Na_2SO_4$ | Agglomerate/Columnar | 1.45 |
| 200K $MgSO_4$ | Acicular | 1.40 |
| 240K Mix | Acicular | 1.30 |



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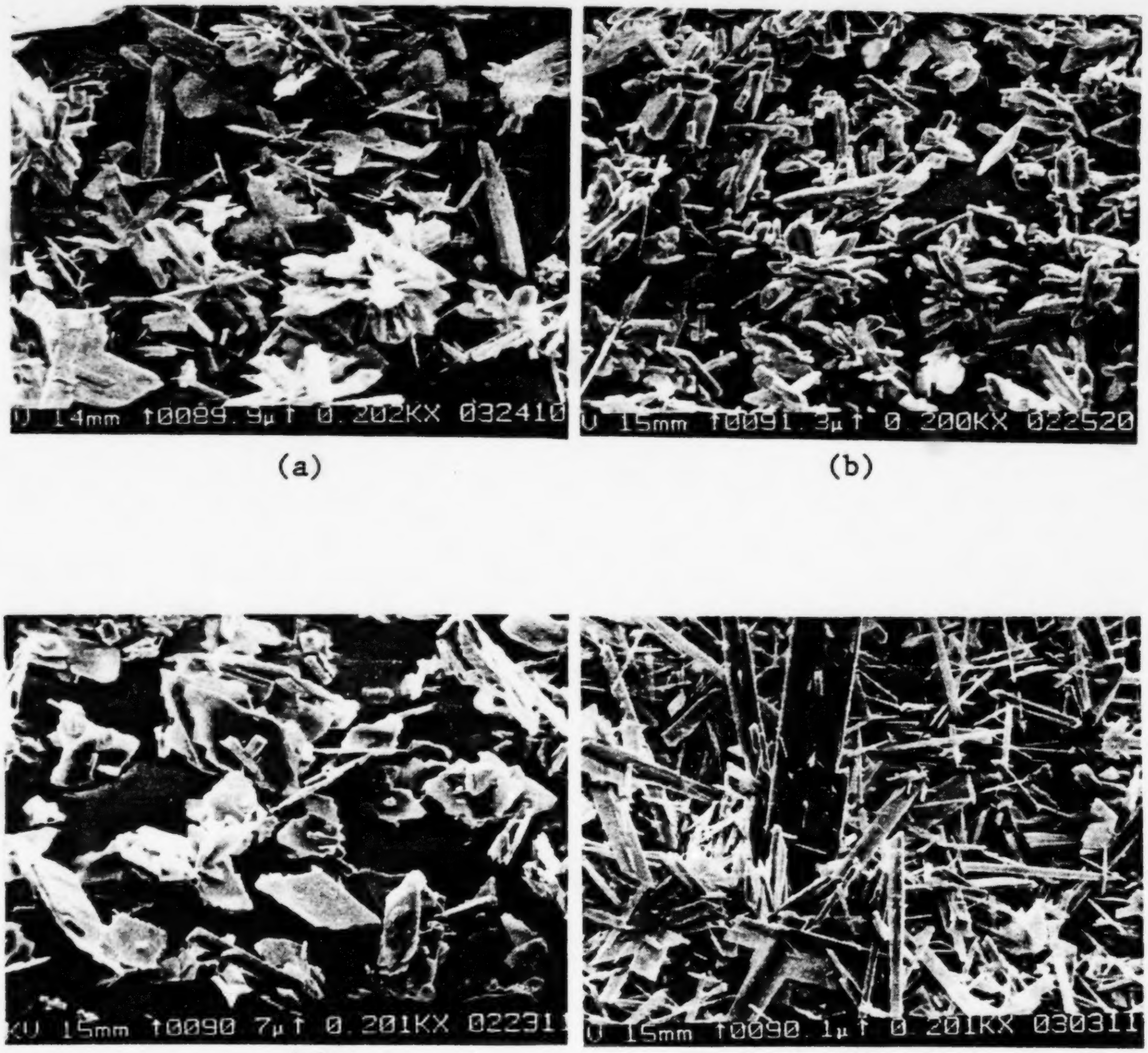
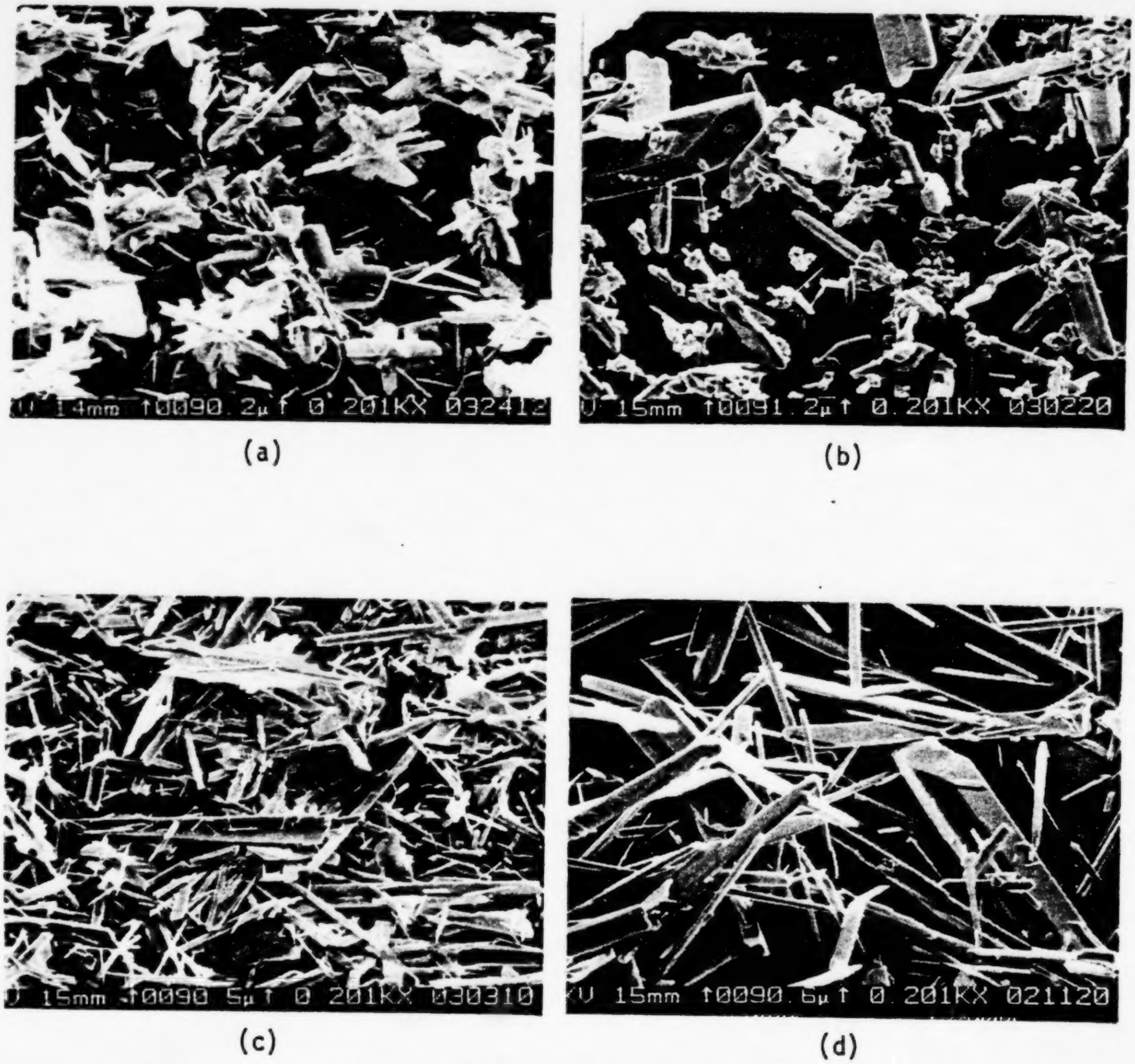

U 14mm ↑0089.9µ↑ 0.202KX 032410
U 15mm ↑0091.3µ↑ 0.200KX 022520
KU 15mm ↑0090.7µ↑ 0.201KX 02231
U 15mm ↑0090.1µ↑ 0.201KX 030311

(a) (b)

(c) (d)

Figure 6. Scanning electron micrographs of gypsum solids

(a) Acicular/agglomerate gypsum from dilute solution.
(b) Columnar/agglomerate gypsum from NaCl (240K)
(c) Lamellar gypsum from $CaCl_2$ (240K)
(d) Acicular gypsum from $MgCl_2$ (240k)


U 14mm ↑0090.2μ↑ 0 201KX 032412
U 15mm ↑0091.2μ↑ 0.201KX 030220
U 15mm ↑0090 5μ↑ 0 201KX 030310
KV 15mm ↑0090.6μ↑ 0.201KX 021120

(a) (b)

(c) (d)

Figure 7. Scanning electron micrographs of gypsum solids

Figure 3-12.
(a) Acicular/agglomerate gypsum from dilute solution.
(b) Columnar/agglomerate gypsum from $Na_2SO_4$ (240K).
(c) Acicular gypsum from $MgSO_4$ (240K).
(d) Acicular gypsum from mixed liquor (240K).

much more lamellar in habit. Of all the inorganic solutions tested, NaCl, $Na_2SO_4$, and $CaCl_2$ had the most effect on crystal habit modification. In both the NaCl and $Na_2SO_4$ liquor solutions the gypsum crystals precipitated were columnar and dendritic even when precipitated at low relative saturations. The more columnar crystal habit is thought to impart better settling and dewatering properties to the respective slurries. Conversely, the gypsum crystals precipitated from the $CaCl_2$ liquor were lamellar in habit, which is not well suited for settling and dewatering.

## PRECIPITATION OF CALCIUM SULFITE HEMIHYDRATE IN HIGH TDS SOLUTIONS

The following section reports the experimental approach and results of the part of the screening study devoted to determining the effects of high TDS soultions on calcium sulfite crystallization.

### EXPERIMENTAL APPROCH

The prevention of localized precipitation is of primary importance in designing and executing precipitation rate experiments. Generally, the mixed suspension-mixed products removal reactor (MSMPR) has been used to measure precipitation rates under steady-state conditions. Satisfactory MSMPR reactor operation requires complete and rapid mixing of the reactant feeds to prevent localized precipitation in the region where the reactant streams mix with the bulk solution. This is especially critical when precipitating slightly soluble salts such as calcium sulfite.

Some initial MSMPR calcium sulfite precipitation tests were conducted at several reagent feed rates. The precipitation rates and the calcium sulfite relative saturations were measured. The precipitated calcium sulfite solids were examined by microscopy. The data from these initial MSMPR experiments indicated that localized precipitation of calcium sulfite was occurring in the MSMPR reactor. Therefore, an experimental approach more closely resembling an actual FGD scrubber system was adopted for the calcium sulfite precipitation rate tests.

Figure 8 shows a schematic of the bench-scale $SO_2$ scrubbing apparatus used to conduct the calcium sulfite precipitation rate tests. The apparatus consisted of a flue gas mixing manifold, gas-liquid contactor, reaction tank, and a calcium carbonate slurry hold tank. Sulfur dioxide gas ($SO_2$) was blended with nitrogen gas and contacted with a calcium carbonate slurry. The $CaCO_3$ slurry was used as a source of alkalinity to neutralize the $SO_2$ absorbed from the gas mixture as shown in Equation 6.

$$CaCO_3(s) + 2SO_2\ (aq.) + 2H_2O \rightleftarrows Ca^{++} + 2HSO_3^- + H_2CO_3 \qquad (6)$$

The calcium from Equation (6) is then available to precipitate calcium sulfite-calcium sulfate solid solution according to the following equation:

$$Ca^{++} + (1-x)SO_3^= + (x)SO_4^= + 1/2H_2O \rightarrow Ca(SO_3)_{1-x}(SO_4)_x \cdot 1/2H_2O \quad (7)$$

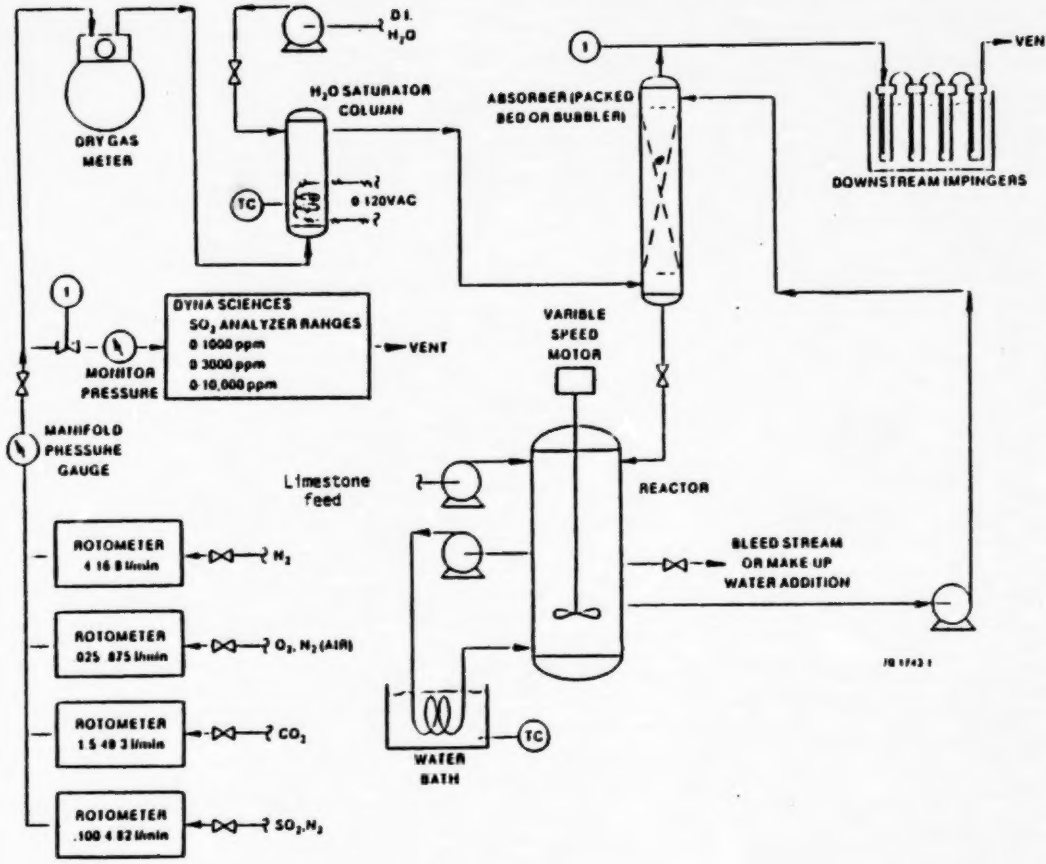


Figure 8. Schematic Diagram of the Bench-Scale $SO_2$ Gas Scrubbing Apparatus Used for Calcium Sulfite Precipitation Studies.

The calcium sulfite precipitation rate was determined directly from the $SO_2$ pickup rate in the bubbler contactor. This assumption is correct only if the reaction tank slurry circulating through the contactor is saturated or supersaturated with respect to calcium sulfite. At the beginning of each test it was first verified that saturation was achieved by periodically analyzing the total sulfite-sulfur concentration until a constant value was reached.

The total sulfite-sulfur and calcium concentrations measured at steady-state and those concentrations measured later from the equilibrium slurry samples were used to calculate the approximate calcium sulfite relative saturations during each test as shown in Equation (8).

$$CaSO_3 \cdot 1/2H_2O \text{ R.S.} \approx \frac{[Ca^{++}][SO_3^{=}]_{\text{steady state}}}{[Ca^{++}][SO_3^{=}]_{\text{equilibrium}}} \qquad (8)$$

## CALCIUM SULFITE PRECIPITATION IN HIGH TDS SOLUTIONS STUDY RESULTS

Seven different high TDS solutions were tested on the bench-scale system and are listed in Table 4. Also shown for each test liquor was the steady-state concentrations of total sulfite and calcium, the calcium sulfite precipitation rate, and the calcium sulfite relative saturation obtained for each test. The dilute solution test was used as a base case for direct comparison with the other high TDS solutions. Of the seven high TDS liquors tested, three contained the common anion chloride (NaCL, $MgCL_2$, $CaCl_2$). The precipitation rate data obtained for each of these solutions is plotted along with the dilute solution data in Figure 9. The high chloride precipitation rate data points all fall around the dilute solution base case indicating that high chloride concentrations had little effect on calcium sulfite precipitation rate. However, a similar plot of the high sulfate test soltuion data, Figure 10, shows some enhancement in the calcium sulfite precipitation rate for a given reltive saturation when compared to the dilute solution base case.

Since large amounts of calcium sulfite seed crystals were retained in the crystallizer during each test, crystal growth and nucleation rates could not be determined individually. Therefore, the effects of high TDS are reported as changes in the overall precipitation rate only. However, it is clear that the precipitation rate of calcium sulfite in high liquors is approximately double the precipitation rate for a given relative saturation when compared to the dilute solution base case and high chloride liquors.

The crystal habit of calcium sulfite precipitating from FGD systems can vary from lamellar crystal shape to crystals resembling rosettes and clusters. It has been noted that the lamellar shaped crystals precipitate more frequently from limestone reagent FGD systems and the rosettes arise primarily from lime-reagent FGD systems.

## Table 4.
## Calcium Sulfite High TDS Precipitation Rate Results[1]

| | | Steady-State Reactor Concentration | | | |
|---|---|---|---|---|---|
| Run No. | Designation[2] | Sulfite mg/L | Calcium mg/L | $CaSO_3 \cdot 1/2H_2O$ Precipitation (mmoles/g-min) | $CaSO_3 \cdot 1/2H_2O$ Relative Saturation |
| 1 | Dilute Solution | 485 | 410 | .008 | 3.05 |
| 2 | Dilute Solution | 660 | 440 | .017 | 4.50 |
| 3 | Dilute Solution | 755 | 485 | .022 | 5.75 |
| 4 | Dilute Solution | 890 | 540 | .025 | 7.40 |
| 5 | Dilute Solution | 965 | 555 | .030 | 8.28 |
| 6 | 240K NaCl | 420 | 295 | .010 | 1.89 |
| 7 | 240K NaCl | 570 | 360 | .013 | 3.20 |
| 8 | 240K NaCl | 620 | 410 | .016 | 4.00 |
| 9 | 240K NaCl | 700 | 440 | .019 | 4.75 |
| 10 | 240K NaCl | 725 | 470 | .022 | 5.25 |
| 11 | 240K NaCl | 775 | 500 | .025 | 5.95 |
| 12 | 240K NaCl | 425 | 320 | .012 | 2.08 |
| 13 | 240K NaCl | 550 | 370 | .017 | 3.14 |
| 14 | 240K NaCl | 595 | 410 | .020 | 3.77 |
| 15 | 240K NaCl | 680 | 440 | .023 | 4.62 |
| 16 | 240K $MgCl_2$ | 925 | 590 | .014 | 2.58 |
| 17 | 240K $MgCl_2$ | 1,355 | 810 | .021 | 5.21 |
| 18 | 240K $MgCl_2$ | 1,420 | 870 | .027 | 5.88 |
| 19 | 240K $MgCl_2$ | 1,520 | 960 | .026 | 6.92 |
| 20 | 240K $MgCl_2$ | 1,525 | 950 | .028 | 6.88 |
| 21 | 50K $CaCl_2$ | 85 | 17,040 | .016 | 6.11 |
| 22 | 50K $CaCl_2$ | 100 | 16,910 | .024 | 6.97 |
| 23 | 50K $CaCl_2$ | 110 | 16,360 | .028 | 7.60 |
| 24 | 50K $CaCl_2$ | 80 | 16,380 | .011 | 4.18 |
| 25 | 24K $Na_2SO_4$ | 3,530 | 510 | .018 | 2.79 |
| 26 | 24K $Na_2SO_4$ | 4,330 | 530 | .026 | 3.54 |
| 27 | 24K $Na_2SO_4$ | 4,700 | 540 | .034 | 3.92 |
| 28 | 24K $Na_2SO_4$ | 5,320 | 525 | .038 | 4.31 |
| 29 | 24K $Na_2SO_4$ | 5,840 | 545 | .042 | 4.92 |
| 30 | 24K $MgSO_4$ | 3,380 | 650 | .031 | 3.89 |
| 31 | 24K $MgSO_4$ | 3,665 | 630 | .038 | 4.08 |
| 32 | 24K $MgSO_4$ | 4,240 | 700 | .041 | 5.25 |
| 33 | 24K $MgSO_4$ | 4,810 | 680 | .048 | 5.76 |
| 34 | 24K Mix | 1,325 | 640 | .021 | 1.50 |
| 35 | 24K Mix | 1,740 | 800 | .025 | 2.45 |
| 36 | 24K Mix | 2,080 | 830 | .029 | 3.00 |

[1] All tests were conducted at 48°C and pH 5.5

[2] K = 1,000 mg/l

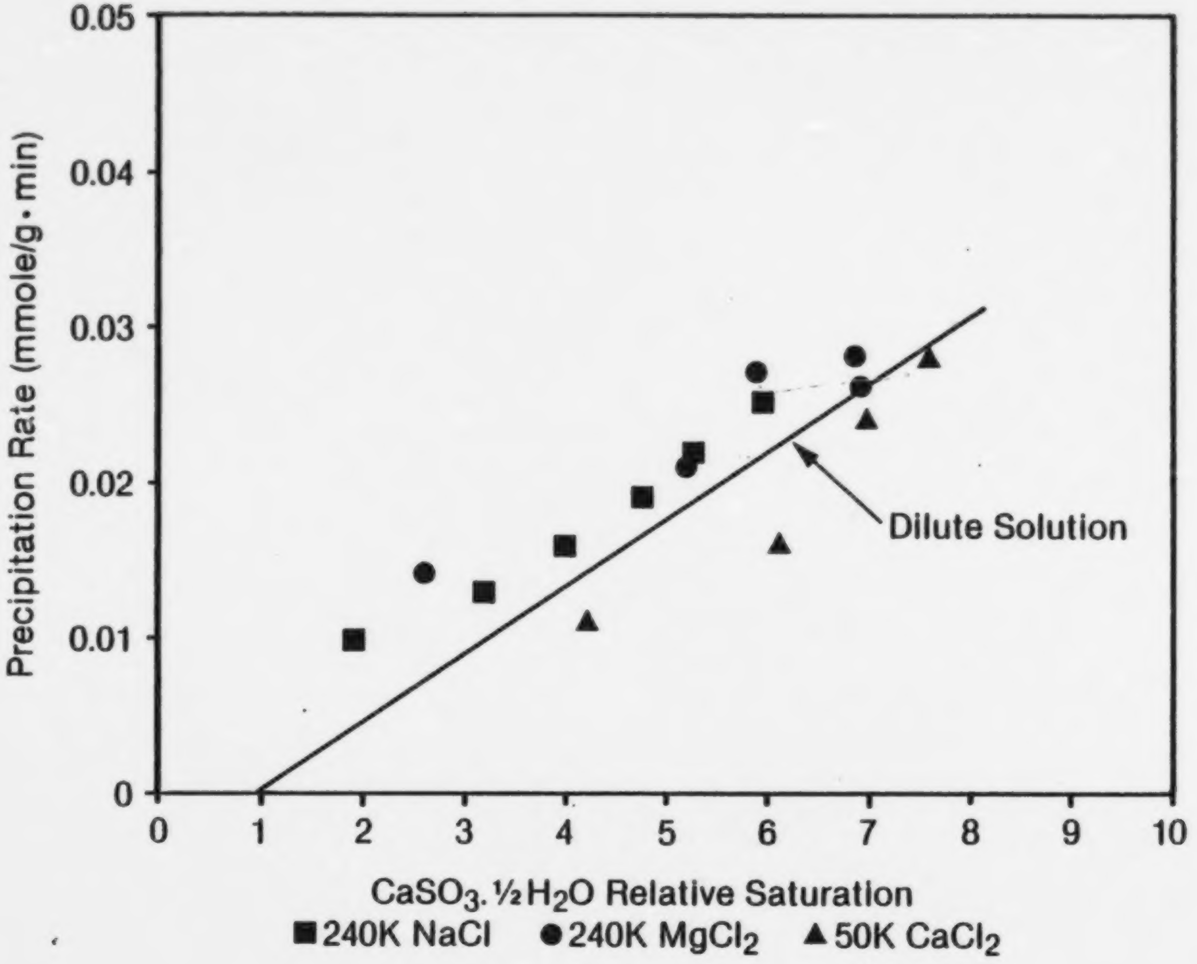


Figure 9. $CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation Results in High Chloride Test Solutions

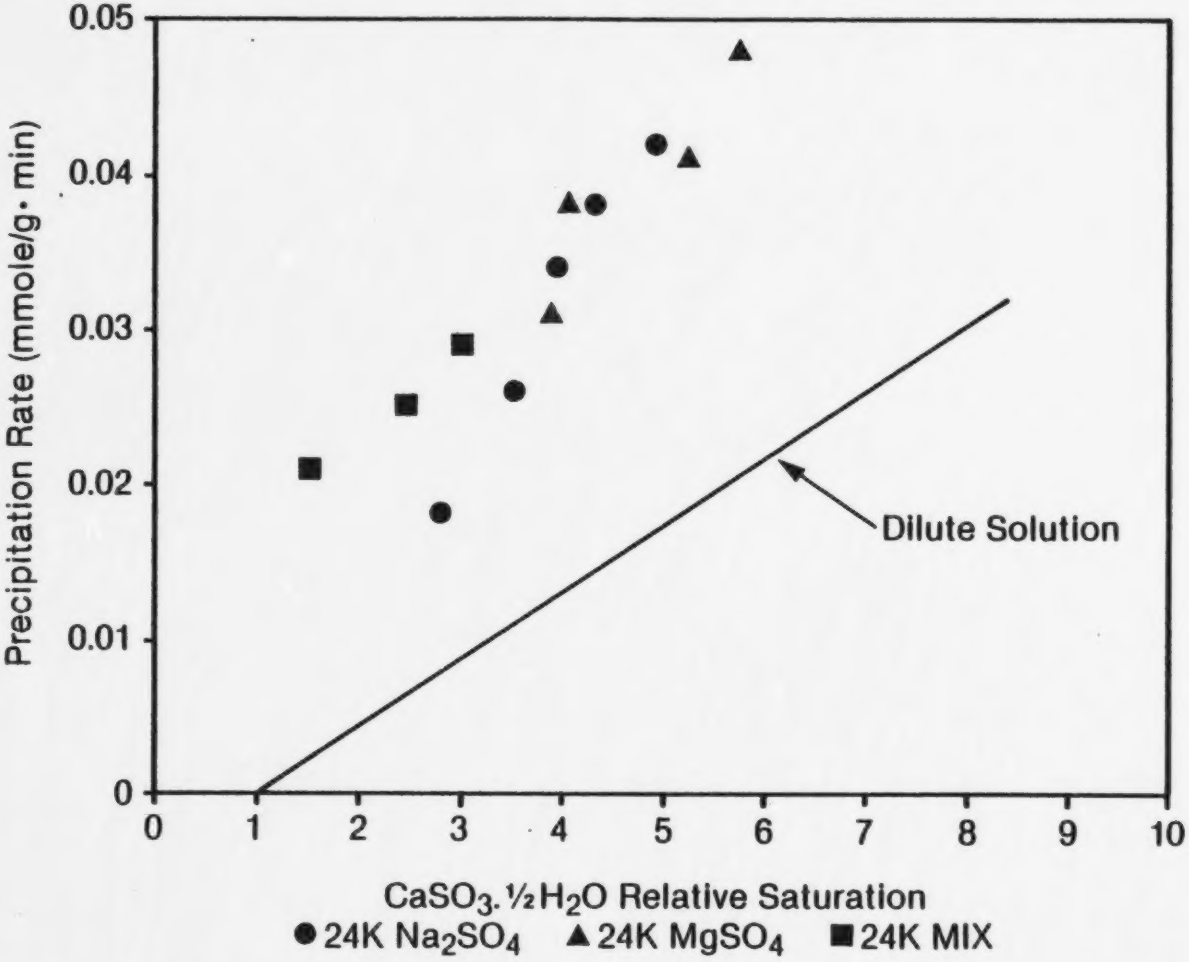


Figure 10. $CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation Results in High Sulfate Test Solutions

Calcium sulfite is known for its poor settling and dewatering properties causing solids disposal problems in some FGD systems. Settling and dewatering characteristics are influenced by many physical factors including particle size and crystal habit. Very little research has been done to determine the effect of high TDS solutions on calcium sulfite crystal habit modification. As part of this screening program, a test sequence was made to screen and evaluate the habit modifying potential of high TDS liquors on calcium sulfite. These tests were carried out by the slow addition of .5 molar solutions of $CaCl_2$ and $Na_2SO_3$ into a stirred, nitrogen purged, 20-liter carboy filled with the high TDS test solution. The reagent addition rate was set at .3 to .4 millimeters/minute and continued for up to 30 hours. The slow reagent addition rate allowed the calcium sulfite relative saturation to increase slowly in the carboy until nucleation occurred. The results of these tests are shown in the photomicrographs in Figures 11 and 12. The crystals precipitated from high chloride liquors are compared with those precipitated from dilute solution in Figure 11. The chloride liquors all produced lamellar type crystals. The NaCl liquor solution produced crystals with a greater length to width ratio resembling crystals more acicular in habit (Figure 11c). The calcium sulfite precipitated from the high sulfate liquors shown in Figure 12 contained no lamellar crystals. The calcium sulfite solids consisted of rod shaped and globular crystals with some foliated growth patterns evident. These crystals appeared to have more mass per unit area than the crystals precipitated from the dilute solution and high chloride liquor solutions.

## SUMMARY AND CONCLUSIONS

### CALCIUM SULFATE CRYSTALLIZATION IN HIGH TDS SOLUTIONS

The results of this screening study showed that the precipitation rate of calcium sulfate was affected by high TDS solution composition. These findings are summarized below.

1. Gypsum precipitation rates in 240,000 mg/l NaCl and $MgCl_2$ solutions were five times greater than in dilute solution for a given relative saturation.

2. Gypsum precipitation rates measured in 240,000 mg/l $Na_2SO_4$, $MgSO_4$, and mixed liquor solutions were 2-3 times greater than in dilute solution for a given relative saturation.

3. The $CaCl_2$ high TDS solution (240,000 mg/l) suppressed the gypsum precipitation rate compared to dilute solution.

4. Calcium sulfate dihydrate was found to be the only hydrate stable in the solutions tested.

5. The crystal shape was found to be affected differently between the high TDS solutions tested.

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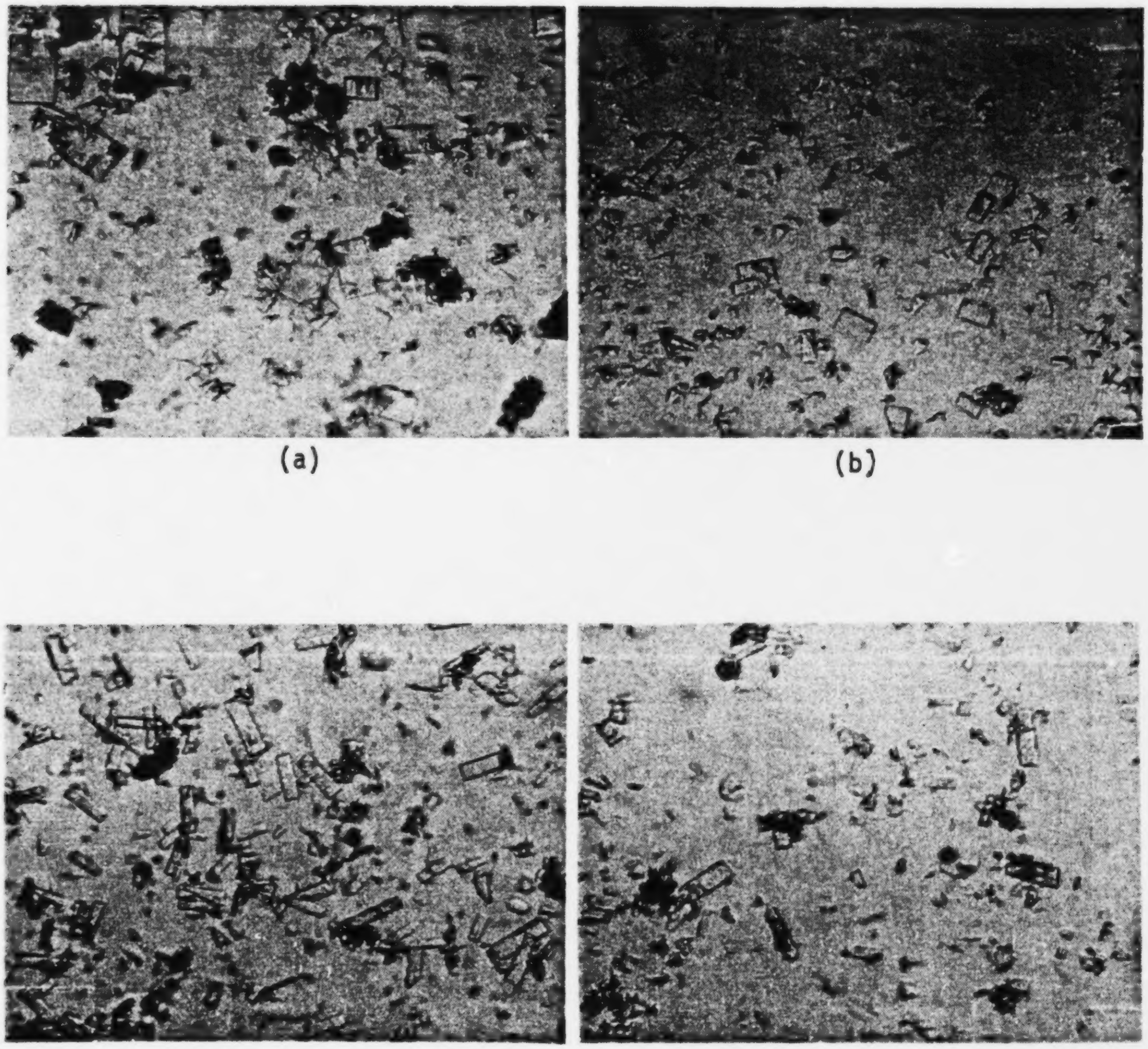


(a)

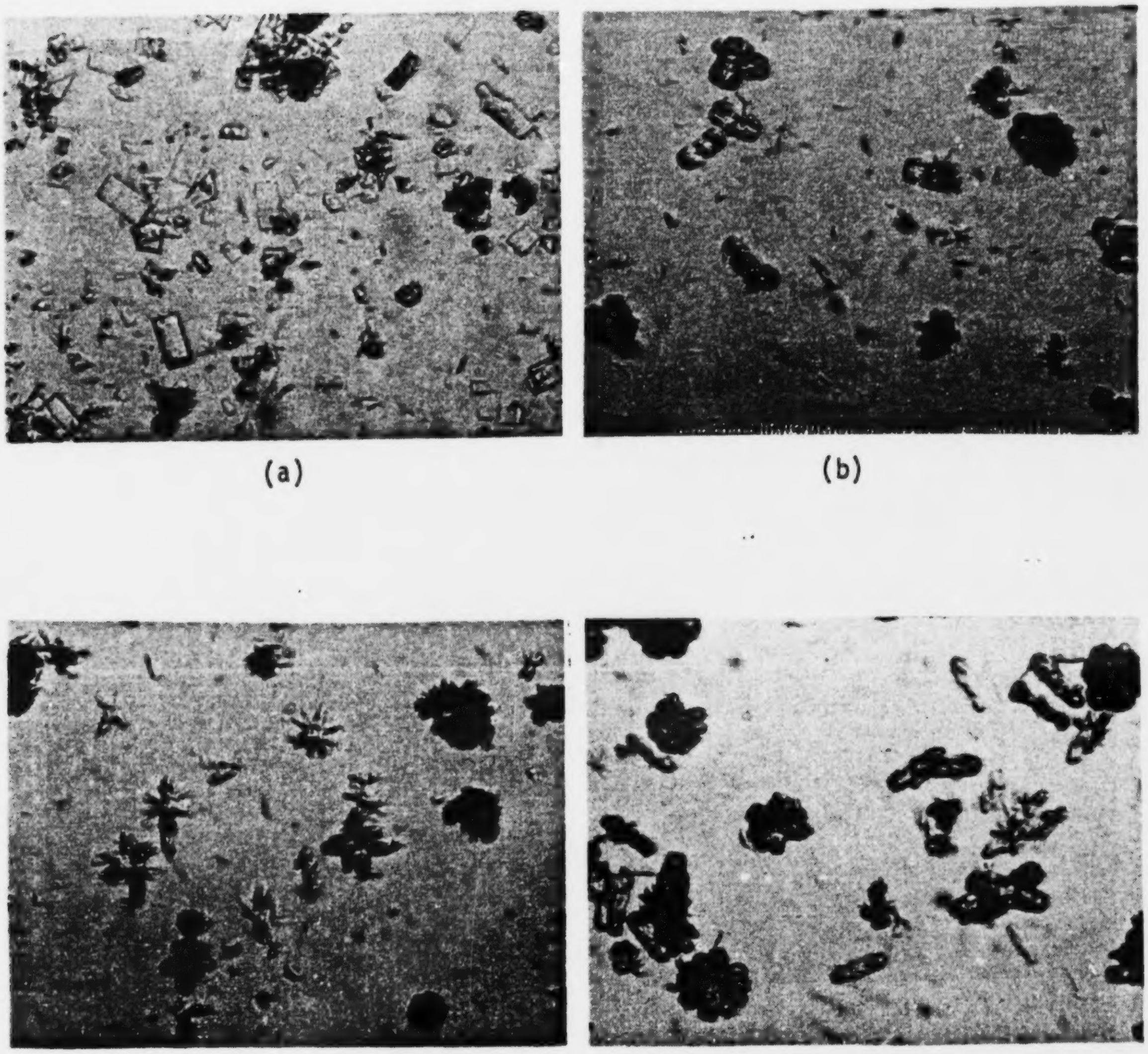
(b)

(c)

(d)

Figure 11. Photomicrographs of Calcium Sulfite Precipitated from HTDS Solutions.

(a) Dilute Solution (b) 50K $CaCl_2$
(c) 240K NaCl (d) 240K $MgCl_2$



(a) (b)

(c) (d)

Figure 12. Photomicrographs of Calcium Sulfite Precipitated from HTDS Solutions.
(a) Dilute Solution (b) 24K $Na_2SO_4$
(c) 24K $MgSO_4$ (d) 24K Mix

The increase in precipitation rate was found to be dependent upon TDS level in tests using a mixture of Na, Mg, Cl, and $SO_4$. Gypsum crystal growth rate measured in this mixed solution composition showed a linear increase in growth rate as a function of TDS level. At a TDS level of 200,000 mg/l the crystal growth rate was enhanced 400% compared to the dilute solution base case.

These results suggest that FGD systems currently operating in the 10,000-25,000 mg/l TDS range are not yet at a TDS level where the calcium sulfate precipitation and growth rates are significantly affected by solution TDS levels. However, these preliminary data indicate that an increase in the TDS level of scrubber liquors containing Na, Mg, Cl, and $SO_4$ may be accompanied by an increase in the gypsum growth rates. An increase in the growth rates of gypsum (for a given relative saturation) in the FGD system can have two potential benefits for FGD operations. First, a larger particle size distribution of scrubber solids should result for a given operating relative saturation. A larger particle size distribution could improve the solids settling and dewatering characteristics of the FGD scrubber slurry. Second, an increase in crystal growth should regulate the gypsum relative saturation in the scrubber at a lower level for a given sulfur dioxide removal. A lower gypsum relative saturation in the reaction tank could decrease the gypsum scaling potential in the absorber.

## CALCIUM SULFITE CRYSTALLIZATION IN HIGH TDS SOLUTIONS

The precipitation rate of calcium sulfite in high TDS solutions was found to depend on solution composition only for those solutions containing sulfate ion. In high TDS solutions of $Na_2SO_4$, $MgSO_4$, and a mixture of Mg, Na, Cl, and $SO_4$, the calcium sulfate precipitation rate was approximately two times the rate measured in chloride based high TDS solutions and in dilute solution. The calcium sulfite precipitation rates were measured over a wide range of relative saturations. Typically, the relative saturation varied from 2 to 8 for each test solution. These relative saturations are typical of those encountered in many FGD systems. These preliminary results indicate that the precipitation rate of calcium sulfite in FGD system will be less affected by increases in the TDS level in the recirculating slurry than that of gypsum.

Solutions containing sulfate were found to influence the calcium sulfite crystal size and habit. Calcium sulfite precipitated in the presence of high concentrations of sulfate were rod shaped or globular with some foliated growth patterns. Whereas, calcium sulfite precipitated in high TDS chloride solutions or in dilute solution were lamellar or acicular in habit. Interpretation of these data are difficult, since these batch screening tests were carried out without knowing the precise relative saturation of calcium sulfite for each test solution. Additional experimentation under steady-state precipitation conditions will be required to accurately evaluate the effect of high TDS solutions on calcium sulfite crystal size and habit.

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# EFFECT OF LIMESTONE GRINDING CIRCUIT ON FGD PERFORMANCE AND ECONOMICS

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## ABSTRACT

Results of several recent EPRI sponsored programs investigating technical and economic issues of limestone preparation for $SO_2$ scrubbing are presented in this paper. Variables important in the selection of a limestone for FGD application are discussed. The most common method used by vendors for sizing limestone ball mills is identified. Correlation of this method with the chemical, physical, and petrographic characteristics of a number of different limestones was investigated.

Pilot-scale testing with a wet ball mill, air-swept ball mill, tower mill, ring roller mill, and hammer mill was conducted with three of these limestones. Selection of the stones was based on the strength of the material. A hard, medium and soft stone were used so that the effect of this variable on each machine's performance could be measured. Data were collected on the performance of these machines in grinding these limestones to various particle size distributions. Product samples collected from each were tested in laboratory equipment to measure the effect of grinding method on limestone dissolution rate.

Full-scale testing at Central Illinois Light Company's Duck Creek Unit No. 1 measured the effect of the limestone mill circuit operation on the product particle size distribution. Testing also quantified the effect of the limestone size distribution on its utilization in the scrubbers. The economic tradeoffs of producing the finer size product were estimated based on data collected during the on-site testing.

## INTRODUCTION

As of March 1983, there were 106 operational utility FGD systems in the United States. An additional 105 systems were under construction or in the planning stage at that time for a total FGD controlled generating capacity of 103,219 MW. Approximately one-half of the existing FGD controlled utility plant capacity use limestone as the alkaline reagent. This fraction is not projected to change by much through the remainder of this century. Based on current FGD industry surveys, the anticipated demand for limestone FGD systems will add an equivalent of six new 500 MW installations per year through 1991.

Using average industry figures, the estimated annual consumption of limestone by utility FGD systems will be almost 40 million tons in 1991. Depending upon the inflation rate for limestone and the average delivered cost, from $700 million to $900 million will be spent annually by the utility industry to purchase this quantity. Factors which affect the cost efficient utilization of this reagent are therefore of significant interest to the utility user. To provide more information in this area, the Electric Power Research Institute (EPRI) has recently sponsored two programs, directed by Dorothy Stewart, which investigate efficient use of limestone in flue gas desulfurization:

- Flue Gas Desulfurization Studies: Limestone Grindability
- Flue Gas Desulfurization Reagent Preparation Study

The first study had two major objectives: 1) determine the range in grindability (ease of grinding) and investigate correlations between limestone grindability and its physical, chemical, and petrographic characteristics; and 2) determine types of tests and data required to size and design ball mill grinding equipment for limestone FGD applications.

The objective of the second study was to develop design and economic information concerning the preparation of lime and limestone for FGD application. Only information on the limestone phase of this program is presented in this paper. Results of pilot-scale grinding equipment testing, lab and bench-scale work, and full-scale utility testing are presented. The paper is organized into two major sections, the first dealing with the grindability program and the second discussing the results of the limestone preparation program.

## LIMESTONE GRINDABILITY

The grindability of a reagent limestone is a characteristic being given ever increasing attention in the optimization of controllable variables in limestone FGD systems. As will be shown in the full-scale testing section of this paper, $SO_2$ removal efficiency and limestone utilization can be increased as the average particle size in the feed is reduced. However, there is an exponential increase in the costs associated with production of smaller particle sizes. And as will be seen in this section, natural variations in stone strength have a major impact on the cost of grinding. This section presents the results of the grindability study, including the selection criteria used to choose the 30 limestones in the study, geologic descriptions for selected limestones, results of the grindability testing, and results of the ball mill sizing survey.

## LIMESTONE SELECTION CRITERIA

The samples selected for this study were chosen primarily to assess the grindability characteristics of a cross section of the major carbonate deposits in the U.S. with commercial potential. No minimum $CaCO_3$ content was specified. In fact, some magnesium limestones and dolomites were purposely included with the high-calcium limestones in order to determine any possible effect of magnesium-carbonate phases on grindability behavior. Of secondary consideration was acquiring stones with a wide variety of physical characteristics, i.e., variable grain size and types and proportions of transported and precipitated constituents.

Because of the nature of carbonate deposits, there are significant lateral and vertical variations in chemical and physical properties over relatively small distances. Therefore, a further selection consideration was the consistency between chemical and physical trends noted within the selected formations and the trends observed at the quarry level. This comparison was made visually, by direct comparison of grab samples of the crushed stone, by conversations with quarry operators and/or other knowledgeable individuals, and through review of available chemical analyses.

Limestone samples were obtained in three ways. A number of the samples selected were on hand in Radian's limestone library in sufficient quantities to conduct all proposed analyses. These samples were screened for consistency as described above. Other samples were newly obtained from quarries identified by R. C. Freas of Limestone Products Corporation or geological survey personnel of appropriate states. In these cases, quarry operators were contacted and asked to supply a minimum 100 pound sample of the formation or unit of interest, along with any pertinent information on the local geologic setting and quarrying operations. The level of detail of this latter information is highly variable, depending primarily on the individual background of each quarry contact. For the remaining samples, available information suggested that the target formations could be too compositionally variable to be sampled by quarry personnel. In these cases, a geologist travelled to the quarry to obtain the material with the quarry personnel's assistance. The thirty limestones selected for study are listed in Table 1. The geologic formation, quarry location, and Radian limestone library code are given for each.

## LIMESTONE SAMPLE DESCRIPTIONS

All of the samples subjected to grindability testing were described with respect to their geologic history and in-hand physical appearance in the published report on this program (1). Descriptions of only three of the limestones are given below. These stones were the ones chosen for study in the Reagent Preparation Program. When possible, details of quarry-specific geology are included with the more general description of each sampled unit's regional characteristics. Any uncertainties regarding sample representativeness are also discussed.

TABLE 1. SELECTED LIMESTONES

| Geologic Formation | Quarry Location | Sample Code No. |
|---|---|---|
| Aragonite | Ft. Pierce, FL | — |
| Manlius | Jamesville, NY | 023-B |
| Monteagle | Tiftonia, TN | 047 |
| Manlius | Jamesville, NY | 023-A |
| Vanport | Butler, PA | 067 |
| Racine Dolomite | Chicago, IL | 051 |
| Beekmantown | Blue Ball, PA | 007 |
| Newala | Birmingham, AL | 043-A |
| Fredonia Mem., St. Gen. | Cave-In-Rock, IL | 069-0 |
| Fredonia Mem., St. Gen | Cave-In-Rock, IL | 069-B |
| Redwall | Peach Springs, AZ | 070 |
| Ocala | Sumterville, FL | 074 |
| Newala | Birmingham, AL | 043-B |
| High Bridge Group | Maysville, KY | 034 |
| Crystal Pass Mem., Sultan | Henderson, NV | 019-A |
| Crystal Pass Mem., Sultan | Henderson, NV | 019-B |
| Salem | Stinesville, IN | 066 |
| Franklin Marble | Sparta, NJ | 075 |
| Bethany Falls, Ls., Swope | Liberty, MO | 072 |
| Dundee | Rogers City, MI | 055-A |
| Murphy | Tate, GA | 073 |
| Edwards | Georgetown, TX | 048 |
| Furnace Creek | Lucerne Valley, CA | 039 |
| Fredonia Mem., St. Gen. | Fredonia, KY | 022 |
| Detroit River | Trenton, MI | 076 |
| Brassfield | Piqua, OH | 010 |
| Iceland Spar | Chihuahua, Mexico | — |
| Kimmswick | Illmo, MO | 071 |
| Dundee | Rogers City, MI | 055-B |
| Undiff. Pennsylvania | Wedone, UT | 068 |

## Monteagle Formation

The Mississippian Monteagle Formation occurs throughout a large area of south-central Tennessee. It is time-correlative with the Ste. Genevieve Formation and the underlying St. Louis Limestone. The Monteagle Formation is extremely variable in its lithologic characteristics.

The Monteagle sample used for this study was collected at the Stone Man Quarry, Tiftonia, TN. The exposed stratigraphic section comprises, from top to bottom, approximately 2 feet of overburden; 18 feet of Bangor Limestone, 48 feet of interbedded Harselle shale and limestones; 180 feet of Monteagle Formation; and 40 feet of St. Louis Formation.

The sample collected from Stone Man was taken from stockpiled material consisting predominantly of the lower 100 feet of Monteagle Formation (high-calcium limestone with minor interbedded shale and chert nodules). A typical sample consists of dark gray, massive, fossiliferous, medium crystalline, medium calcarenite.

## Salem Formation

The Salem Formation is a Mississippian limestone that contains the thickest units of high calcium stone exposed in Indiana. The formation crops out from Montgomery County to the Ohio River and into Kentucky. It is overlain by the St. Louis Limestone and underlain by the Harrodsburg Limestone.

The Salem Formation was deposited in a shallow marine environment characterized by frequent fluctuations in shoreline. This depositional setting resulted in a geometrically complex network of lenticular bodies of fossil-rich material within an overall wedge-shaped formation. Total formational thickness may, in places, exceed 80 feet.

The Salem sample used in this study was obtained from Indiana Cal-Pro, which produces high-calcium limestone from an underground mine located about 0.5 miles southwest of Stinesville, IN. Here, a 91 foot thick section of Salem Limestone is overlain by approximately 16 feet of St. Louis Limestone and underlain by 35 feet of Harrodsburg Limestone. The mined stone is extremely consistent in both physical and chemical characteristics. A typical hand-specimen is described as a light gray, massive, fossiliferous, medium calcarenite.

## Kimmswick Formation

The Ordovician Kimmswick Formation (subgroup in Illinois) crops out mainly along the Mississippi River from northwestern Illinois to southwestern Missouri and is also exposed along the White River in Arkansas. Formational thickness decreases to the south. In Illinois, thicknesses vary from about 150 to 200 feet, but in Missouri the range is 25 to 120 feet.

The Kimmswick Subgroup in Illinois includes the Wise Lake and Dunleith Limestone units, of which the former is the more widely quarried. Compositionally, the Kimmswick varies from fine-grained high-calcium limestone to cherty and argillaceous limestones and dolomites.

In Missouri and Arkansas, the Kimmswick is a major source of high-calcium stone. It typically contains only minor impurities (principally chert) and exhibits only local dolomitization.

The Kimmswick sample used in this study was obtained from West Lake Quarry and Materials Company in Illmo, Missouri. Quarry-specific details were not obtained; however, the sample supplied is high-calcium limestone composed of approximately 96 percent $CaCO_3$. A typical sample is a light gray to tan, massive, fossiliferous, medium calcarenite.

## GRINDABILITY TEST RESULTS

The grindability of the limestone samples was determined using a laboratory ball mill procedure developed at Radian. The procedure was patterned after the Hardgrove method for measuring coal grindability and was intended to produce relative grindability data for the rapid and inexpensive analysis of a large number of different limestone samples. Briefly, the test method uses a specific size jar mill, specific size and amount of ceramic grinding media, and specific size distribution and amount of limestone feed. The limestone is dry ground at a preset mill rpm for three timed periods such that the total number of mill revolutions per test can be calculated. The ground limestone product from each timed grinding is screened to determine the weight percent passing through a USA Standard No. 200 mesh sieve. A plot is then constructed of mill revolutions versus percent material passing through 200 mesh. The number of revolutions required to grind 80 percent of the sample to -200 mesh is determined from the plot. The grindability index for each sample tested is then defined as the quotient of 50,000 divided by the number of mill revolutions required to grind the sample to 80 percent passing through a 200 mesh sieve.

Figure 1 presents the results of the grindability tests made on each of the 30 limestones in the study. The grindability index is inversely proportional to the ease of grinding with the hardest or highest strength stones having the smallest index and the lower strength stones having higher numbers. As the figure shows, the range of indices measured for the limestones tested was from 2.1 (hardest stone) to 15.5 (softest stone). These results indicate that there is a significant variation in limestone strength in the U. S. population of stones. Stone strength or grindability is a major factor affecting the size of ball mills. This variable is therefore an important consideration in designing and operating limestone preparation equipment.

To assess correlations between grindability and other physical, chemical, and petrographic characteristics, each limestone was analyzed for: $CaCO_3$, $MgCO_3$, and acid insoluble material; crystalline phases; dissolution rate; grain size; specific gravity; and thin section petrography. Six samples were also tested using the Bond Work Index method. (The Bond Work Index is the most widely used measurement for sizing ball mills, as will be discussed later.) The results from the tests using the grindability index and the Bond Work Index procedures were compared to assess the sensitivity of the two methods to differences in grindability and to determine any relationship between the two methods. Figure 2 presents a graph of the observed relationship between Bond Work Index and grindability index.

Correlations between grindability and the other variables were evaluated by measuring the strength of correlation coefficients for linear relationships and the probability of those relationships being statistically significant. The only significant correlations observed were between grindability index and: 1) Bond Work Index, 2) percent $CaCO_3$, 3) percent acid insolubles (inerts), and 4) percent quartz. The correlation between grindability index and Bond Work Index was very strong and very significant, which validates results from the laboratory procedure. The statistical significance of the correlation does not indicate a cause-and-effect relationship, however, since both methods are direct measures of grindability. Although the correlations between grindability index and percent $CaCO_3$, inerts, and quartz are statistically significant, the correlations are not very strong. And, percent

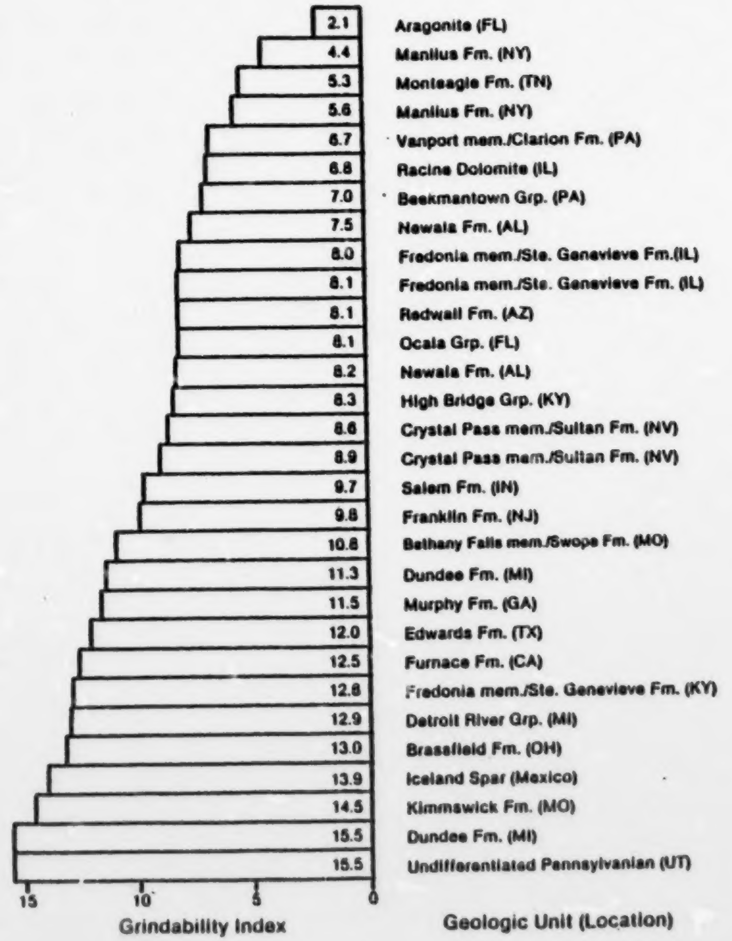

Figure 1. Range of Grindability Indices Observed

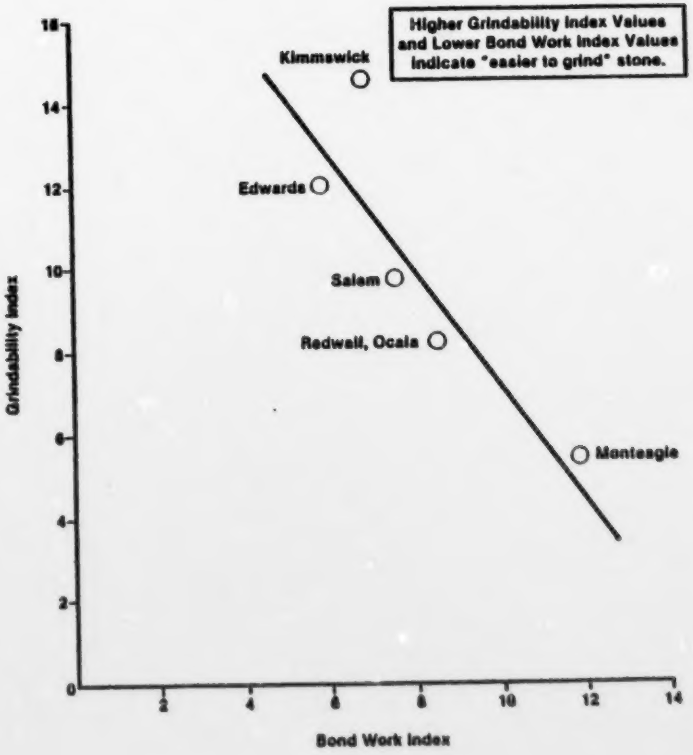

Figure 2. Relationship of Grindability Index With Bond Work Index

$CaCO_3$, inerts, and quartz are themselves strongly correlated; i.e., they are interrelated and are not independently varying. In this study, no physical, chemical, or petrographic characteristics of limestones were correlated strongly enough with grindability to be a predictor of grindability.

## Survey of Ball Mill Sizing Techniques

Since its development, the ball mill has found use in a wide variety of grinding applications. Operational characteristics of this grinding machine have made it by far the most popular selection for limestone FGD. Despite the fact that ball mills have been in use for over 100 years, techniques for designing and sizing them have had little basis in theory. As a result, grinding and particle size reduction has developed more as an art than a science for not only the ball mill, but for most other size reduction equipment. The sizing of ball mills has been largely a question of applying empirical equations or factors based on accumulated experience (2).

Results of the equipment manufacture and literature survey indicate that the sizing-by-energy method, developed principally by Fred C. Bond, is currently the most popular approach used for designing limestone ball mills for FGD applications. This technique assumes that the energy per ton to break a given feed size to a desired produce size is constant for a selected limestone. Then, the energy per ton and a scale-up relationship involving mill diameter are used to size the mill. The energy input to the test mill is measured from power and grinding time, scaled to the production mill diameter, and the production mill length estimated from an equation relating power to mill length and diameter.

These relationships form the basis for sizing mills using the Bond Work Index approach. With this method, a standard laboratory test procedure is used to gather information to calculate the Bond Work Index by an empirical formula. This Work Index is then used to estimate the required mill power per ton of product by the following equation:

$$E = 10\ WI \left[ \left( \frac{1}{P_{80}} \right)^{0.5} - \left( \frac{1}{F_{80}} \right)^{0.5} \right] \tag{1}$$

where: $E$ = kilowatt-hours per ton,

$WI$ = Bond Work Index,

$P_{80}$ = micron size that 80% of the product passes, and

$F_{80}$ = micron size that 80% of the feed passes.

This required specific energy (E) is then used to size the mill based on a power-to-size relationship derived from mechanical analysis of a tumbling mill (3):

$$W = K\rho L D^{2.5} \tag{2}$$

where: $W$ = power to rotate a rumbling mill,

$K$ = a constant for a given set of mill conditions,

$\rho$ = ball density,

$L$ = mill length, and

$D$ = mill diameter.

And since,

$$E = W/Q \tag{3}$$

where: $Q$ = desired production rate,

substituting fives:

$$Q = K\rho LD^{2.5}/E \tag{4}$$

This relationship is used to choose the mill length and diameter to give the desired product rate.

Therefore, the required mill power per ton of product (specific grinding energy) and production rate determine the size of the mill. Since the specific grinding energy is directly proportional to Bond Work Index, the effect of limestone grindability on specific energy can be estimated. Using Figures 1 and 2, the range of Bond Work Indices for the 30 test stones is approximately 5 to 14. Substituting these into Equation 1 and using a $P_{80}$ of 36 microns (equivalent to a product with 90% passing 325 mesh) and an $F_{80}$ of 8,500 microns (∿1/2 inch top size raw limestone), the specific energy required to grind stone with a Work Index of 5 is 8 kW-hrs/ton and for a stone with a Work Index of 14 is 22 kW-hrs/ton. Limestone strength can therefore have a significant effect on the amount of energy required to grind the material to a size distribution typical of that used in a wet limestone scrubber.

As an example of the effect that stone strength has on the size of the ball mill and motor, two mill systems were designed for a conceptual 500 MW plant firing a high sulfur (3.5% by wt) coal. The mills were sized to prepare 24 hours worth of limestone for the scrubbers with the unit at maximum boiler load in one 8-hour shift. The mill system was capable, therefore, of producing 90 tons per hour of limestone, of which 90 percent would pass a 325 mesh screen. For the soft stone with a Bond Work Index of 5, the mill requires 940 hp. The mill grinding the stone with a BWI of 14 requires approximately 2600 hp. Actual motor horsepowers will be higher due to motor efficiency and gear drive losses for both cases.

Mill length and diameter are chosen based on the previously described relationship between these dimensions and the required mill horsepower (Eq. 4). Each mill manufacturer has his own application philosophy which dictates the length to diameter (L/D) ratio for a given set of conditions.

However, it is known that as the diameter of the mill is increased for a given application, the specific energy to grind the material to the desired product size decreases. There is a limitation to this effect, though. For limestone preparation in FGD applications, the mill length is usually 15 to 30 percent larger than mill diameter.

A representative size for a mill which requires 940 hp for grinding is 14 feet in length and 11 feet-6 inches in diameter. And a mill requiring 2600 hp for grinding is 18 feet in length and 15 feet-6 inches in diameter. In terms of annual power costs, the mill grinding the softer stone will consume 2.0 x $10^6$ kW hrs. of electricity (65% plant capacity factor) costing $90,000 annually, and the mill grinding the harder stone will consume 5.6 x $10^6$ kW hrs. of electricity costing $250,000 annually. Plant power costs are assumed to be 45 mils/kW-hr.

Based on these examples, limestone grindability has a significant effect on mill circuit economics. More detailed cost information is being generated at the time of this paper as part of the FGD Reagent Preparation program. The scope of the cost study covers not only the effect of stone grindability but also the effect of product size distribution and type of grinding machine. The results of the cost study will be available in the final report issued on the Reagent Preparation Study.

## FGD REAGENT PREPARATION STUDY

The preparation of lime and limestone reagents for conventional wet scrubbing FGD systems has typically not been a unit process for which there is readily available design inforamtion. To obtain information that utilities could use in planning or designing new FGD systems or in optimizing existing grinding equipment, EPRI initiated this study. This paper discusses the results available to date on the phase of the program concerning the preparation of limestone for wet FGD applications.

### PROGRAM OBJECTIVES

The objective of this program was to obtain technical and economic data useful for the selection and design of limestone grinding systems. The type of equipment studied included the major designs available for commercially grinding limestone. The size of the equipment tested was chosen so that scale-up to commercial size was possible.

Both wet and dry media grinding were studied. The four basic grinding machines examined were: 1) ball mill, 2) ring roller mill, 3) hammer mill, and 4) tower mill.

### RESULTS OF PILOT SCALE GRINDING TESTS

To gather design information to allow scale-up to commercial size, testing was conducted at equipment manufacturers' test facilities using pilot-scale equipment. The ball mill and ring roller mill tests were performed at Kennedy Van Saun Corporation's Danville, Pennsylvania test plant. The hammer mill testing took place at Mikropul Corporation's Summit, New Jersey test plant. And the tower mill testing was conducted at the Koppers Company test facility in York, Pennsylvania.

Three different limestones were tested to investigate the effect of limestone strength or grindability on the performance and costs of the mills. The limestones selected for this study were also investigated as part of the Limestone Grindability program discussed earlier. They were the Kimmswick, Salem, and Monteagle stones. The following sections discuss the results of the testing in order of mill type.

## Ball Mill Testing

The ball mill study included pilot-scale testing of:

- an open circuit wet ball mill,
- a wet ball mill in closed circuit with a hydrocyclone,
- a wet ball mill in closed circuit with a high frequency vibrating screen, and
- an air-swept ball mill in closed circuit with a centrifugal classifier.

The ball mill used for open and closed circuit wet ball milling tests was an overflow discharge type mill having a shell inner diameter of 3 feet and an effective length of 5 feet. During testing, the mill was fitted with corrugated liners, giving an effective mill diameter of 2.69 feet. The mill was driven by a 15 hp hydraulic motor. The grinding charge consisted of almost 3000 pounds of 2 inch, 1-1/2 inch, and 1 inch diameter steel balls. The mill was operated at 34 rpm and a strain gauge was used to measure mill pinion shaft torque which was used to compute mill pinion shaft power. The hydrocyclone used for wet, closed circuit ball mill testing had an inner cylinder diameter of 3 inches, an apex diameter of 5/8 inch, and a vortex finder of 3/4 inch diameter. Two screen cloths were used with the high frequency vibrating screen; one with a screen opening of 111 microns and the other with a screen opening of 156 microns. The air-swept ball mill had an inner shell diameter of 3-1/2 feet and a length of 5 feet. This mill was fitted with corrugated liners also, giving it an effective inner diameter of 3 feet. The mill was driven by a 25 hp motor. The grinding media consisted of about 4300 pounds of 1-1/2 inch, 1-1/4 inch, 1 inch, and 1/2 inch diameter steel balls. The mill was operated at 34 rpm and mill power was determined from a watt meter connected to the mill motor and corrected for drive train losses. The classifier used to close circuit the mill was a centrifugal "H" classifier. A fan was used to generate the air flow necessary to convey the ground stone from the mill to classification.

The test variables for each test circuit were:

Open Circuit Wet Ball Mill

- three limestone types
- three mill slurry percent solids
- three mill feed rates
- two mill feed size distributions

Closed Circuit Wet Ball Mill with the Hydrocyclone and Vibrating Screen

- three limestone types

Air-Swept Ball Mill

- one limestone type
- three air flow rates

In addition to gathering actual operating information on the performance of the pilot wet ball mill operating in closed circuit with a hydrocyclone or screen, this circuit was modelled using the fundamental mathematical relationships which have been developed describing grinding in ball mills. This approach was taken for budget and time reasons since a comprehensive test program would be very expensive, even at the pilot-scale. It was important to verify the validity of the model and to do this, some testing was geared specifically toward validation. Laboratory testing was also included in the program to determine the breakage kinetics parameters for each limestone.

The data analysis and assessment methodology consisted of comparing data generated from the actual tests performed on the wet ball mill with model-simulated data to demonstrate the validity of the model. Then, the model was used to generate further data over a broader range of operating conditions. These results were then analyzed to determine the important relationships used to evaluate ball mill performance which are those between specific grinding energy, throughput, and product size.

The model was validated for each of the three limestones at various throughputs and at two levels of feed size for the Salem and Monteagle stones. Figure 3 presents one comparison between actual test results and model predicted values for the Kimmswick stone. This level of agreement was also seen for the other two stones which satisfactorily validated the ability of the model to predict the performance of the 3 ft. x 5 ft. wet ball mill over a wide range of operating conditions.

Figures 4, 5 and 6 present the results of the open and closed circuit ball mill simulations for the Kimmswick, Salem, and Monteagle stones, respectively. The results display the relationship between specific energy and product particle size passing 200 mesh. Specific energy is defined as mill

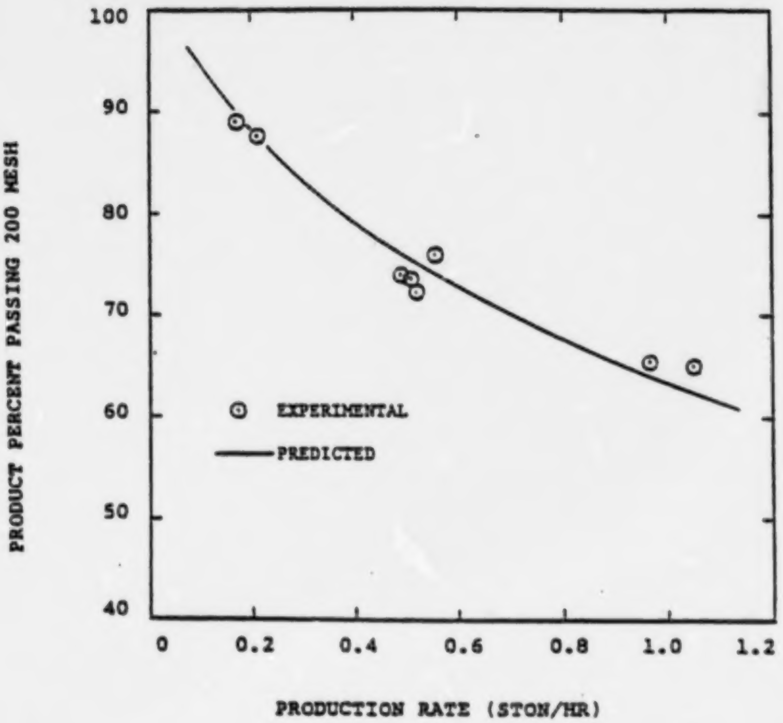

Figure 3. Production Rate vs. Product Fineness for Kimmswick Limestone Grinding in the KVS 3 ft. x 5 ft. Wet, Open Circuit Ball Mill

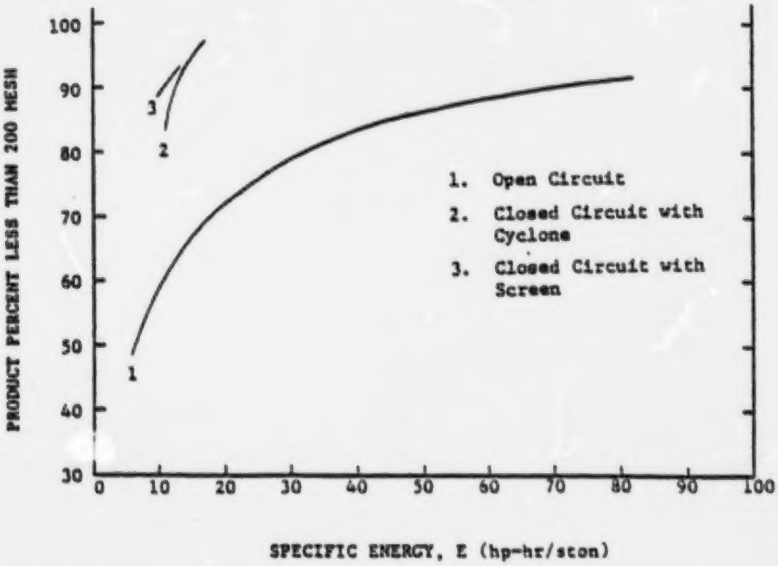

Figure 4. Specific Energy Requirements for Size Reducing 3/8" x 0 Kimmswick Limestone in the Wet Ball Mill

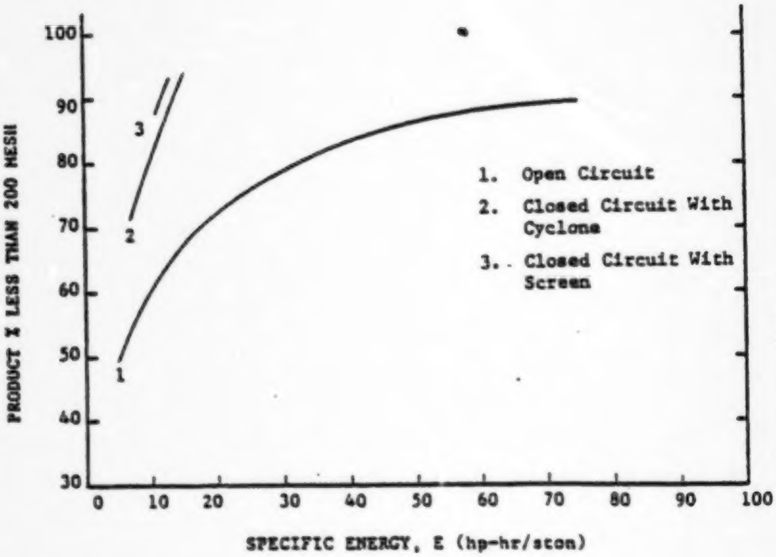

Figure 5. Specific Energy Requirements for Size Reducing 3/8" x 0 Salem Limestone in the Wet Ball Mill

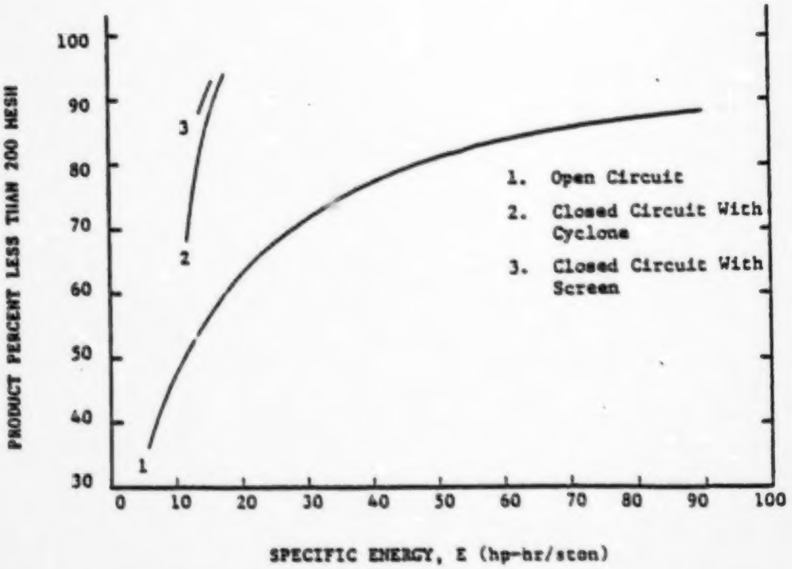

Figure 6. Specific Energy Requirements for Size Reducing 3/8" x 0 Monteagle Limestone in the Wet Ball Mill

drive shaft power divided by circuit throughput. The results show the marked advantage of closed circuit grinding compared to open circuit grinding for all three stones. Recall that a reduction in specific energy not only decreases the mill power consumption but also the size of the mill to produce equivalent rates.

About 70 hp-hr/ton are required to grind the Kimmswick stone from a 3/8" x 0 feed size to a product size distribution of which 90 percent would pass 200 mesh with the mill operating in an open circuit mode. With the harder Monteagle stone, the open circuit mill would require about 100 hp-hr/ton to do the same reduction. Closing the circuit with either hydrocyclones or screens reduced the specific energy for the Kimmswick stone to 10 to 12 hp-hr/ton, depending on the type of classifier. A similar reduction was seen for the Monteagle. This improvement is due to the classifier:

1) removing coarse particles from the mill product and returning them for further grinding, and

2) removing particles from the circuit that are already fine enough, thereby preventing overgrinding.

The screen classifier gave slightly better performance than the hydrocyclone based on limited classifier testing performed at the KVS test facility. The screens were able to give a sharper classification than the hydrocyclone. The result is that slightly lower (by about 10 percent) specific energy requirements were seen for equivalent product sizes.

The results also show the difference between the required energy to produce a given particle size due to stone grindability. Comparing the Kimmswick and Monteagle stones, the model predicts about 12 hp-hr/ton are required for the softer Kimmswick and 16 hp-hr/ton for grinding the harder Monteagle stone to a 90 percent passing 200 mesh size. Using the Bond Work Index method, the energy predicted to grind the Kimmswick from a similar feed size to product size is 14 hp-hr/ton and for the Monteagle it is 25 hp-hr/ton. The lack of agreement between the model and Bond methods for the Monteagle stone is probably due to the inability of the Bond method to account for the greater effect of feed size on mill productivity for a hard stone versus a soft stone.

Table 2 compares the results of the model simulating grinding two different feed sizes of the Monteagle and Kimmswick to a product of which 90 percent passes 200 mesh using a hydrocyclone. It is seen from this table that decreasing the feed size for a "hard" limestone such as the Monteagle causes a significant decrease in mill power relative to the same change for a "soft" limestone such as the Kimmswick.

## Air-Swept Ball Mill Test Results

The test work performed on the pilot air-swept ball mill was much more limited than the testing with the wet ball mill. The reason for this is that the application of this type of grinding device for preparing limestone for FGD use is almost nonexistent. When compared to wet ball milling in

Table 2. EFFECT OF LIMESTONE FEED SIZE ON MILL SPECIFIC ENERGY TO PRODUCT 90 PERCENT PASSING 200 MESH

| Limestone | 95 Percent Passing, In. | Specific Energy, hp-hr/ton |
|---|---|---|
| Monteagle | 3/8 | 16.1 |
| | 1/4 | 13.7 |
| Kimmswick | 3/8 | 12.7 |
| | 1/4 | 12.2 |

identical situations, the dry mill requires approximately 30 percent greater energy input according to past experience. The reason for this is that ground material coats the balls inside the mill and cushions the ball-to-ball impact, reducing grinding efficiency. Also, there is no advantage to producing the limestone in a dry form, since it must be eventually added to an aqueous slurry in the scrubber reaction tank. In addition, the feed material to the mill must be dried completely to prevent caking and packing of the limestone inside the mill. Finally, grinding limestone to very fine particle sizes typical of that required for limestone FGD systems even further decreases the grinding efficiency of the dry ball mill compared to a wet mill. This is caused by agglomeration of the already finely ground material, preventing ball-to-ball nipping of individual particles which is the primary size reduction mechanism.

Table 3 presents the results of the dry ball mill tests which were made using the Monteagle limestone. The Monteagle stone was chosen since the harder limestone would present less of a problem for the mill in terms of the powder cushioning effect.

TABLE 3. AIR-SWEPT BALL MILL TEST RESULTS

| Mill Throughput, lbs/hr | Air Flow, acfm | % Passing 200 Mesh | Specific Energy, hp-hr/ton |
|---|---|---|---|
| 300 | 1000 | 90 | 188 |
| 580 | 1500 | 78 | 101 |
| 1030 | 1900 | 71 | 61 |

The results of the tests indicate that the air-swept ball mill was capable of producing a suitable FGD product size distribution at very high specific energies. The reason for high energy requirements could be due to too low of an air flow to either effectively convey the limestone out of the mill or to promote efficient classification in the classifiers. However, the fan power represented at least 25 percent of the total power requirements. Therefore, while increasing fan power may increase classifier and overall mill circuit efficiency, the specific energy required by an air-swept ball mill is expected to be substantially higher than the closed circuit wet ball mill.

## Ring Roller Mill Test Results

The grinding media for the ring roller mill was 5 inch steel balls. The mill has an adjustable internal classifier, three adjustable load springs and is driven by a fifteen hp motor through a V-belt drive. Mill power was determined from a watt meter connected to the mill motor. The ring roller mill grinds under dry conditions. Air is used to sweep fines from the mill.

Testing with the ring roller mill was limited for the same reasons as was the dry ball mill testing. Table 4 presents results of the ring roller mill tests with the Kimmswick and Monteagle stones.

TABLE 4. RING ROLLER MILL TEST RESULTS

| Limestone | Air Flow acfm | Throughput lbs/hr | % Passing 200 mesh | Specific Energy hp-hr/ton |
|---|---|---|---|---|
| Monteagle | 840 | 220 | 57 | 105 |
| " | 1140 | 470 | 51 | 54 |
| " | 1640 | 680 | 37 | 45 |
| Kimmswick | 820 | 260 | 61 | 87 |
| " | 1100 | 440 | 55 | 55 |
| " | 1600 | 1060 | 49 | 30 |

The results indicate that the ring roller mill was not capable of producing an FGD quality grind, even at very high specific energies. As with the air-swept ball mill, this may be due to insufficient air flow to convey the fines from the mill and/or poor classifier performance.

## Hammer Mill Testing

A fine grinding hammer mill was tested at Mikropul Corporation's Summit, New Jersey test facility to investigate its ability to produce a limestone size suitable for FGD use. The limestone is ground by contacting fresh feed with a high speed rotor to which are attached fixed "T" head hammers. Rotor speed was varied over a range of from 5000 to 7000 rpm, giving extremely high peripheral speeds. Air sweeps the fine material from the grinding chamber upward to a centrifugal type mechanical classifier which may be operated at various speeds. In addition, the length of the classifier blades can be changed to investigate the effect of blade length on system performance. Rotor amps, classifier amps and fan power were monitored to calculate total system horsepower. Fan power was approximately one-half of total system power.

All three test stones (the Monteagle, Salem, and Kimmswick) were studied in the hammer mill. Mill operating conditions which were varied included rotor speed, classifier speed, and classifier blade length. Table 5 presents selected results from the testing with Monteagle and Kimmswick limestone.

The results show that the hammer mill was capable of producing a very fine grind (100 percent passing 200 mesh) for both the Monteagle and Kimmswick stones. Reducing rotor speed, classifier speed, and classifier blade length resulted in a coarser product, but the resulting increase in throughput lowered the specific energy. There was a noticeable effect on specific energy due to stone strength. Specific energy was anywhere from 20 to 40

TABLE 5. HAMMER MILL TEST RESULTS

| Limestone | Rotor Speed rpm | Classifier Speed rpm | Blade Length | % Passing 200 Mesh | Specific Energy hp-hr/ton |
|---|---|---|---|---|---|
| Monteagle | 6000 | 2000 | Long | 100 | 68 |
| " | 6000 | 1000 | Long | 93 | 48 |
| " | 5000 | 2000 | Long | 99 | 69 |
| " | 5000 | 1000 | Long | 88 | 44 |
| " | 6000 | 1000 | Short | 78 | 43 |
| " | 5000 | 2000 | Short | 98 | 47 |
| Kimmswick | 6000 | 2000 | Long | 100 | 56 |
| " | 6000 | 1000 | Long | 98 | 33 |
| " | 5000 | 2000 | Long | 99 | 58 |
| " | 5000 | 1000 | Long | 93 | 30 |
| " | 6000 | 1000 | Short | 81 | 31 |
| " | 5000 | 2000 | Short | 99 | 27 |

percent lower when grinding the Kimmswick stone compared to the Monteagle. The hammer abrasion index was measured for the Monteagle and Kimmswick stones also. The Monteagle index was 175 microns/5 pounds of material ground and the Kimmswick index was 105 microns/5 pounds. These numbers are useful in predicting the wear rate and therefore the life of the hammers. In general, the specific energies which were measured for each test were much higher than those for equivalent size products produced in closed circuit wet ball milling.

The test with the Kimmswick stone at a rotor rpm of 5000, classifier rpm 2000, and with short classifier blades that produced a grind at a specific energy that approaches to within a factor of 2 the performance of the closed circuit wet ball mill. This suggests that with further tuning, the hammer mill may be able to produce an equivalent particle size with specific energies approaching those required in the wet ball mill. It should be noted that this was seen only for the softest stone, though.

## Tower Mill Testing

A pilot-scale tower mill was tested at Koppers Company, York, Pennsylvania facility. The tower mill is a wet grinding device that relies on a ball charge to accomplish the necessary breakage and size reduction of a particular material. However, unlike the ball mill which tumbles the ball charge, the tower mill consists of a vertical cylindrical chamber which contains the ball charge. Fresh feed and classifier oversize material is fed to the top of the chamber. A rotating screw flight agitates the ball charge, which grinds the limestone in this case by a combination of ball-to-ball, ball-to-screw, and pebble-to-pebble attrition. The finely ground particles that are generated are carried upward through the chamber and overflow into the coarse classifier. Overflow from this classifier is fed to a spiral classifier. The product is taken from the spiral classifier, and oversize material is recycled back to the grinding chamber. Mill throughput and classifier operation were varied to produce different product size distributions for the Monteagle, Salem, and Kimmswick stones tested. The test approach taken with the tower mill was somewhat different than with the other mills. Instead of running a comprehensive evaluation of mill operating conditions, the circuit was controlled to produce specific size distributions for direct comparison to the closed circuit wet ball mill. Table 6 presents the results of the tests.

TABLE 6. TOWER MILL TEST RESULTS

| Limestone | Product Size<br>% Passing 200 Mesh | <br>% Passing 325 Mesh | Specific Energy hp-hr/ton |
|---|---|---|---|
| Kimmswick | 93 | 65 | 6 |
| Kimmswick | 100 | 88 | 11 |
| Salem | 93 | 68 | 6 |
| Salem | 100 | 88 | 12 |
| Monteagle | 97 | 70 | 10 |
| Monteagle | 99 | 85 | 14 |

Examining the results in the table indicate that the tower mill is capable of producing a very fine particle size (99+ percent passing 200 mesh) at what are lower specific energies than the closed circuit wet ball mill. As with the other mills, stone strength also affects the specific energy required to achieve a given product size for the tower mill. Also, significantly greater energy is required to produce a finer particle size, as was expected.

## LABORATORY TESTING

The work at CILCo's Duck Creek Station (discussed in the next section) demonstrated the beneficial effect that a fine particle size distribution has on full-scale FGD performance. The major objective of this laboratory work was to document the effect that different grinding devices can have on FGD system performance exclusive of particle size effects. The hypothesis tested was that different mills would produce products with different fissure characteristics due to different breakage mechanisms. Different fissures might result in different limestone dissolution rates, even for samples with identical particle size. If this is true, then a mill which creates a faster dissolving product would not have to be designed to obtain the same size product as a mill which creates a slower dissolving product.

### Approach

The approach taken was to use laboratory-scale equipment to determine the effect different grinding mills would have on FGD performance. Two different bench-scale systems were employed: 1) a limestone reactivity setup developed previously for EPRI (Figure 7), and 2) a bench-scrubber arrangement which scrubs a simulated flue gas (Figure 8).

The nucleus of the reactivity apparatus is a stirred tank reactor with pH and temperature control. For each test, a known amount of limestone was added and allowed to dissolve while maintaining reactor solution pH at the

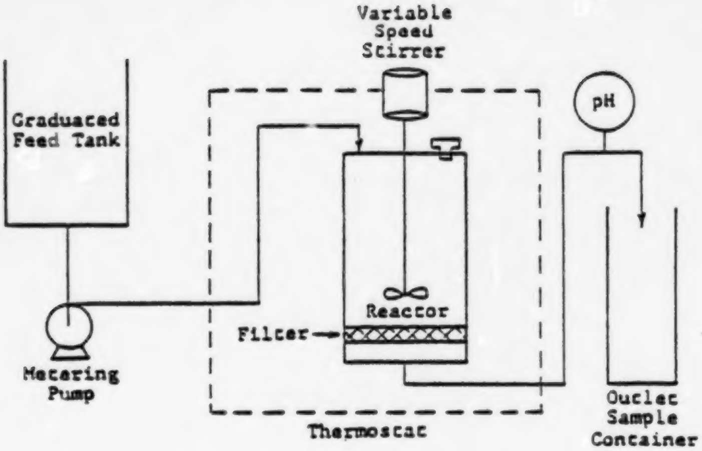

Figure 7. Limestone Reactivity Apparatus

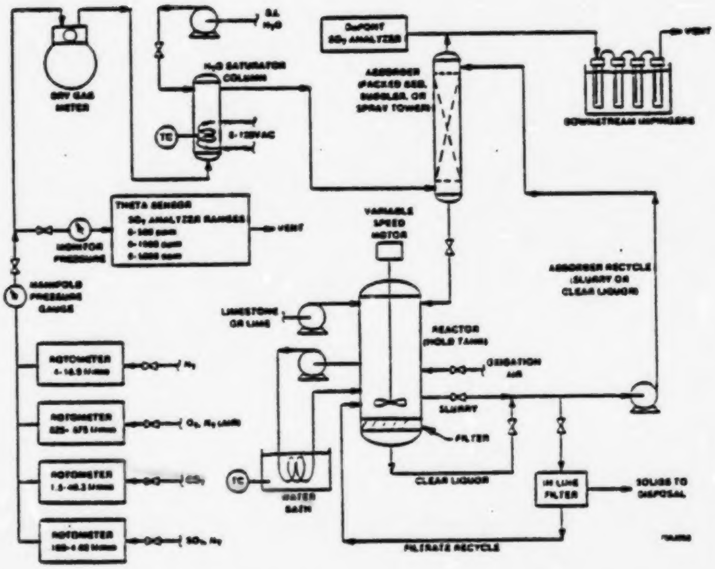

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Figure 8. Schematic Diagram of the Bench-Scale FGD System

desired setpoint by controlled addition of 0.025N HCl stock solution. Liquid is withdrawn through a filter at the same rate the acid solution is added, thus creating a liquid flow-through, batch-solids reactor. By monitoring the outlet flow rate and calcium concentration, the cumulative calcium dissolved and the dissolution rate can be computed as a function of time. Dissolution rate reported at 50 percent of the limestone dissolved has been a useful method of comparing different limestone types and particle size distributions.

The bench-scale wet scrubber equipment consisted of a one-inch diameter countercurrent gas-liquid contactor and a two-liter reaction tank for limestone dissolution and sulfur salt precipitation. A simulated flue gas containing $SO_2$, $O_2$, $N_2$, and $CO_2$ was fed to the bottom of the contactor at a controlled rate of 0.5 scfm. Slurry from the reaction tank was pumped to the contactor at a rate equivalent to an L/G of approximately 50 gal/1000 acf. Temperature of the reaction tank slurry was maintained at 50°C (122°F) by an external heater. Limestone was fed to the reaction tank as a 20 percent slurry to maintain a pH of 5.8. The duration of each run was at least six hours, with some runs being extended to three days. Limestone utilization was the primary measurement made to document the effect of particle size on FGD system performance since the $SO_2$ removal was roughly equivalent for all 5.8 pH runs.

The first series of experiments were designed to show that the limestone reactivity and bench scrubber test results are consistent with trends measured at the full-scale facility. Once this was demonstrated, the remainder of the experimental work was conducted on the bench reactivity apparatus.

## Results

A comparison of bench-scale and full-scale test results are reported in Table 7. The trends measured in the lab are consistent with those measured at CILCo, although the bench scrubber does not exactly duplicate the CILCo limestone utilization. The range in utilization was 58 to 93 percent (coarse to fine) at CILCo and 67 to 80 in the bench scrubber. At CILCo, the medium and fine grinds achieved very similar results, while the bench scrubber results showed the medium grind to be more of a mid-point in utilization. The bench reactivity tests showed the dissolution rate (measured at 50 percent limestone dissolved) of the fine and medium grinds to be very close and substantially greater than that for the coarse grind. This trend is similar to the full-scale results.

TABLE 7. COMPARISON OF BENCH-SCALE AND FULL-SCALE LIMESTONE* UTILIZATION RESULTS

| Limestone Size (% passing 325 mesh) | Bench Reactivity Limestone Dissolution Rate at 50% Dissolved (mg/min) | Bench Scrubber Limestone Utilization (%) | CILCo Limestone Utilization (%) |
|---|---|---|---|
| 90 (fine) | 19.2 | 80 | 93 |
| 80 (medium) | 18.8 | 75 | 89 |
| 70 (coarse) | 11.7 | 67 | 58 |

*All tests conducted with Kimmswick limestone and 5.8 pH setpoint.

Once the bench reactivity test had been demonstrated to reflect trends observed in full-scale systems, a test matrix was set up to measure differences in limestone ground in different mills. The following variables were investigated:

Limestone Source - Monteagle (hard)
Kimmswick (soft)

Size Fraction - +325, -200 mesh (∿56 μ mass mean diameter)
+400, -325 mesh (∿44 μ mass mean diameter)

Grinding Mill Type - wet ball mill
tower mill
air-swept ball mill
ring roller mill
hammer mill

The results of the tests are summarized in Table 8. The only variable found to have a statistically significant effect on dissolution rate was the particle size. Neither the type of mill nor the type of limestone was found to have a major effect on the dissolution rate. Consider, for instance, the Kimmswick 325-400 mesh runs. The range of dissolution rates for three different mills was 5.2 to 5.5 mg/min with an 0.2 difference found in a duplicate set of runs. The same size fraction with the Monteagle limestone yielded a 5.0 to 5.4 mg/min range in dissolution rate. On the other hand, the 200-325 mesh samples gave 3.3 to 3.8 mg/min dissolution rates for both limestones and four different mill types.

TABLE 8. RESULTS OF LIMESTONE REACTIVITY TESTS

| Mesh Size | Limestone Source | Mill Type | Dissolution Rate mg/min at 50% dissolved |
|---|---|---|---|
| 325-400 | Monteagle | ASBM | 5.4 |
| 325-400 | Monteagle | Hammer | 5.0 |
| 325-400 | Monteagle | WBM | 5.2 |
| 325-400 | Monteagle | Tower | 5.3 |
| 325-400 | Kimmswick | WBM | 5.3 |
| 325-400 | Kimmswick | Tower | 5.4 |
| 325-400 | Kimmswick | Tower | 5.2 |
| 325-400 | Kimmswick | RRM | 5.5 |
| 200-325 | Monteagle | Hammer | 3.4 |
| 200-325 | Monteagle | WBM | 3.6 |
| 200-325 | Monteagle | WBM | 3.6 |
| 200-325 | Monteagle | Tower | 3.8 |
| 200-325 | Kimmswick | Hammer | 3.3 |
| 200-325 | Kimmswick | Tower | 3.7 |

Based on these results, it appears that a limestone grinding mill should be selected based on capital and operating costs required to produce a reasonably fine limestone particle size distribution (80 to 90 percent passing 325 mesh). It does not appear that differences in breakage mechanisms of the mills considered in this study had a measurable effect on FGD system performance when equivalent limestone size fractions were tested.

CILCO DUCK CREEK FULL SCALE TESTING

In 1982, the Central Illinois Light Company (CILCo) initiated a program to improve performance of the FGD system at its Duck Creek Station. As part of the overall effort, Radian, EPRI and CILCo decided that improving limestone grindability circuit performance should be examined as a means of improving FGD system performance. Three aspects of the FGD system were used as guidelines to measure the performance: $SO_2$ removal, limestone consumption, and mist eliminator scaling.

System Description

The Duck Creek Station generates about 400 MW of electrical power while at full load. The four rod-deck scrubber modules treat about 1.4 million acfm (130°F, saturated) of flue gas which contains about 2500 ppm $SO_2$ prior to entering the scrubbers. Reagent preparation and waste disposal are common to all modules. Figure 9 shows a simplified flow schematic.

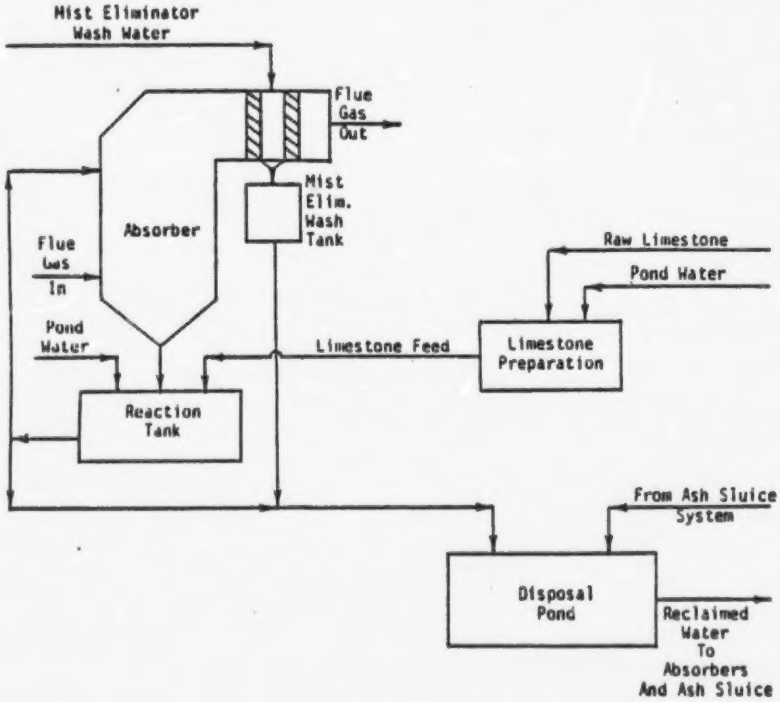

Figure 9. Duck Creek FGD System

A 10 ft. x 18 ft. wet ball mill (rated capacity of 40 tons per hour) grinds the limestone, and four 10-inch diameter hydrocyclones were initially used to control product size distribution. Product slurry is stored in a 125,000 gallon tank prior to being fed to the scrubber reaction tanks. Columbia Quarry supplies the limestone, which is mined from the Kimmswick formation.

A pH feedback loop controls the limestone feed rate to the reaction tanks. The pH setpoint in each tank can be maintained within ±0.05 units with the on-off controller. The four 150,000 gallon reaction tanks provide necessary time for dissolution of the limestone and precipitation of calcium-sulfur salts. The slurry solids level is maintained at about 12 percent by bleeding slurry to the disposal pond and returning clarified liquor from the pond.

Reaction tank slurry is pumped to the top of the scrubbers at a rate of about 15,000 gpm. The slurry contacts the flue gas countercurrently with the seven rod-decks providing the turbulence required to achieve $SO_2$ removal. At full-load conditions, the liquid-to-gas ratio is about 40 gal/1000 acf, and the gas-side pressure drop is about 12 inches w.g.

A two-stage horizontal mist eliminator is located downstream of the last rod deck in each absorber to remove entrained slurry. Periodic washing removes collected solids. Flue gas exits the system without reheat through a lined wet stack.

## Approach

The approach taken in this phase of the program was to modify grinding circuit operating variables, monitor the effect on limestone product particle size distribution, and then measure the effect the change in limestone product had on FGD system performance. Limestone mill/classifier variables which were examined include:

- mill throughput
- mill slurry solids
- level of ball charge in mill
- top-size of balls in mill
- raw limestone feed size
- diameter of classifier barrel
- classifier pressure drop (or throughput)
- solids content in classifier feed
- diameter of vortex finder and apex

The only equipment modifications were the changes in the vortex finder, apex, and classifier barrel. Total capital expenditures were only about $7,000.

## Results

Time did not permit extensive parametric testing, so it is not possible to isolate and measure the effect of each variable on mill/classifier system performance. However, the changes which had the greatest effect on limestone product particle size at Duck Creek were all related to the classifier:

- reduction in classifier barrel diameter from 10 inches to 6 inches

- reduction in the slurry solids in the classifier feed from ~50 to ~45 wt%.
- increase in classifier pressure drop from 15 to 30 psi (increase in angular velocity within hydrocyclone)

The modifications in mill/classifier operation resulted in a finer limestone product particle size distribution. Prior to any changes, 86 percent of the product passed a 200 mesh screen and 73 percent passed 325 mesh screen. After the system had been optimized, 99 percent of the product passed 200 mesh and 90 percent passed 325 mesh.

The effect the finer limestone had on FGD system performance is summarized in Table 9. At a pH setpoint of 5.8, the limestone utilization increased from below 60 percent to above 90 percent as the product size decreased. An alternate method of summarizing the results shows that $SO_2$ removal (measured at 85 percent limestone utilization) increased from about 72 percent to about 84 percent as the grind improved.

TABLE 9. RESULTS OF LIMESTONE GRINDING SYSTEM OPTIMIZATION

| Grind | Particle Size % <200 mesh | Particle Size % <325 mesh | Limestone Utilization at 5.8 pH (%) | $SO_2$ Removal at 85% Utilization (%) |
|---|---|---|---|---|
| Coarse | 86 | 70 | 58 | 72 |
| Medium | 94 | 81 | 89 | 82 |
| Fine | 99 | 90 | 92 | 84 |

The improved mill/classifier performance allows the Duck FGD System to operate at a higher pH while still maintaining better limestone utilization than previous operation. The finer limestone particle size distribution resulted in: 1) increased $SO_2$ removal efficiency, 2) decreased limestone consumption for equivalent time of operation, and 3) decreased scaling on the mist eliminator.

Increased $SO_2$ Removal--With the finer limestone grind, the FGD system could maintain a higher pH setpoint than originally designed. Prior to the optimization, the design pH setpoint had been 5.6. The $SO_2$ removal at full load was about 74-77 percent (82~85 percent required by regulation). The fine grind allows the system to operate at 5.8 pH and achieve 82-84 percent $SO_2$ removal at full load.

Decreased Limestone Consumption--Prior to the mill/classifier optimization, the 5.6 pH setpoint resulted in about 77 percent limestone utilization. This will result in limestone consumption of 160,000 tons per year if the plant operates at the CILCo goal of 75 percent capacity factor. (Note also that the $SO_2$ removal is below that required by regulation under these conditions). After optimization, the limestone utilization was 93 percent at 5.8 pH, which translates to 144,000 tons per year of limestone consumed. The savings of 16,000 tons per year of limestone is worth about $220,000 per year.

Decreased Mist Eliminator Scaling--Prior to the mill/classifier optimization program, the mist eliminators had to be manually cleaned every four days to prevent excessive solids buildup. This cleaning required about 400 maintenance hours per week, and part of the flue gas had to bypass the FGD system because of leaking isolation dampers. The improved limestone utilization which resulted from the finer limestone, combined with improved wash water quality, resulted in greatly decreased mist eliminator fouling. Both good limestone utilization (>85%) and wash water subsaturated with respect to gypsum were required. Neither can be used solely to improve mist eliminator fouling. These improvements virtually eliminated the need for manual cleaning of the mist eliminators.

## CONCLUSIONS

Conclusions drawn from the limestone grindability and limestone reagent preparation programs can be summarized as follows:

- Grindability can vary widely from one limestone formation to the next.
- The limestone grindability lab method correlates well with the Bond Work Index as a measure of limestone strength. Other physical properties did not correlate strongly with BWI.
- Grindability (BWI) is widely used to size ball mills for FGD application. The extremes of stone strength found in the grindability study result in a factor of 3 difference in the operating costs (specific energy) and a significant difference in size of mill required.
- BWI does not effectively account for the effect changes in feed size of harder limestones has on specific energy requirements.
- The tower mill and wet ball mill operating in a closed circuit offer the least energy intensive options for grinding limestone. Pilot investigations showed the tower mill to have an advantage in specific energy requirements.
- If designed to produce equivalent PSD's, the type of mill does not affect limestone dissolution rate.
- PSD is an extremely important design and operating variable in limestone FGD systems. Scrubber $SO_2$ removal, limestone consumption, and reliability are all affected.

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